KINETIC STUDIES ON THE ZIRCONIUM / HAFNIUM TETRA CHLORIDE-ALKALI CHLORIDE SYSTEM AND FABRICATION OF A REACTOR FOR FRACTIONAL DECOMPOSITION OF THE COMPOUNDS
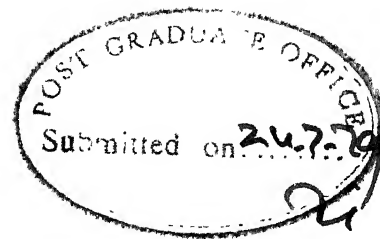## $Na_2\,Zr\,Cl_6$ and $Na_2\,Hf\,Cl_6$

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY
in
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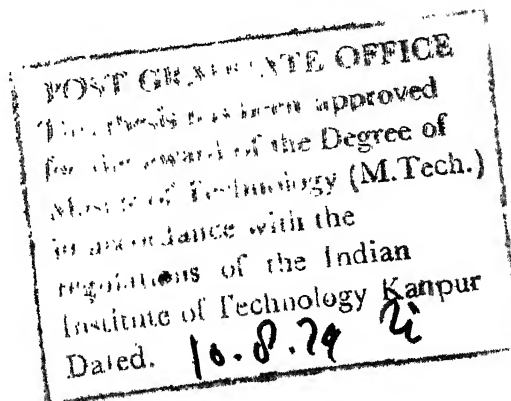JULY 1979

CERTIFICATE

Dated: July;1979

Certified that this work on the ' Kinetic studies
on the Zr(or Hf)Cl_4- alkali chloride system and fabrication
of a reactor for fractional decomposition of the compounds
Na_2ZrCl_6 and Na_2HfCl_6 ' has been carried out under our
supervision and that it has not been submitted else where
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LIST OF SYMBOLS

d_o = Size of NaCl particle, mm

F = Fraction reacted

H_R^o = Heat for decomposition of the reaction, Kcal./mole

j = $K_j.t$, from Jander's, equation 12, Chapter 2,

K' = Reaction rate constant, equation 8, Chapter 2.

M_r = Molicular weight of solid reactant

MCl = Alkalimetal chloride, where M = K, Rb or C_s.

P_{ZrCl_4} = Partial pressure of $ZrCl_4$, mm of Hg.

P = Partial pressure, mm of Hg.

T = Temperature in °K.

t = time in hours

X_{Cl_4} = Tetrachloride where X = Z_r or Hf

y = thickness of product layer in mm.

r = Density of solid reactant, gm/cc.

1 = Stoichiometry factor

ABSTRACT

Kinetic studies on the Zr (or Hf) Cl_4^- alkali-
chloride system has been one of the objectives of this
investigation. It is carried out by means of trans-
piration technique on a packed bed of the NaCl. The
effect of time, temperature and pressure on the reaction
rate is reported. Effects of presence of KCl in the bed,
in weight percents, on the reaction rate has also been
indicated.

Fractional decomposition of $Na_2 Zr Cl_6$ and Na_2
$Hf Cl_6$ leads to the separation of the two elements
Zirconium and Hafnium due to the differences in their
stabilities. To achieve this, a reactor has been designed,
fabricated and assembled. Definite operational data
can be obtained by carrying out studies on this reactor.

CHAPTER- ONE

INTRODUCTION

1.1 General:-

Zirconium ores always have Hafnium, usually from one half to several percents depending upon the type of mineral. These elements are similar in nature and behave like isotopes of the same element. This is due to the same electronic structure of the two elements and nearly equal ionic radii due to lanthanide contraction on the ionic radius of Hafnium. Thus during processing of ores these two elements always remain together unless Hafnium is removed by special methods of seperation. Hafnium does not effect the mechanical strength or corresion resistance of Zirconium. However, when a Zirconium alloy is used in nuclear reactors, as a cladding material of the fuel rods, even traces of Hf are very harmful as the element increases the neutron absorption cross section for some elements.

The usage of Beryllium, Magnesium & Aluminium is precluded due to their low melting points. Thus it becomes necessary to use Zirconium and reduce Hafnium to less than 200 ppm to

TABLE -I   Thermal neutron absorption cross section of elements
            used as core construction materials (Hafnium as a
            a control rod material).

Element	Absorption cross section (barns) *	Melting point (°C)
Beryllium	0.010	1280
Magnesium	0.063	651
Zirconium	0.180	1845
Aluminium	0.230	660
Niobium	1.1	2415
Iron	2.53	1539
Molybdenum	2.5	2625
Copper	3.69	1083
Nickel	4.46	1455
Titanium	5.8	1725
Hafnium	105.0	2222

Reference :- S.M. Shellon, Metallurgy of Zirconium (Book),
          McGraw Hill Publication.

          * Barns is a unit for nuclear cross section
            1 Barn = 10^{-24} cm^2

produce Zirconium of nuclear grade.

A very large number of techniques are available for removal of Hafnium, These fall mainly in two categories, viz. the physical methods and the chemical methods. The former includes processes such as solvent extraction, fractional crystallization etc. These physical methods have been more sucessful, and therefore, are the basis of the industrial processes so far. Chemical methods involving, chemical reactions(usually involving various halides) have not yet been sucessfully exploited for production of nuclear grade Ziconium.

Solvent extraction process extensively used to day to remove Hafnium from Zirconium is shown in a flow drawn in the fig. no. 1. The first step in process is the production of Zr (Hf) tetrachloride by high temperature gaseous chlorination of either Zircon- carbon composites or Zirconium carbide previously prepared by the carbothermic reduction of Zircon. The chloride is purified, often in the presence of reducing agents to yield a high grade anhydrous zirconium (hafnium) tetrachloride material. The anhydrous tetrachloride is subsequently dissolved in an aquous medium and the composition of the resul-
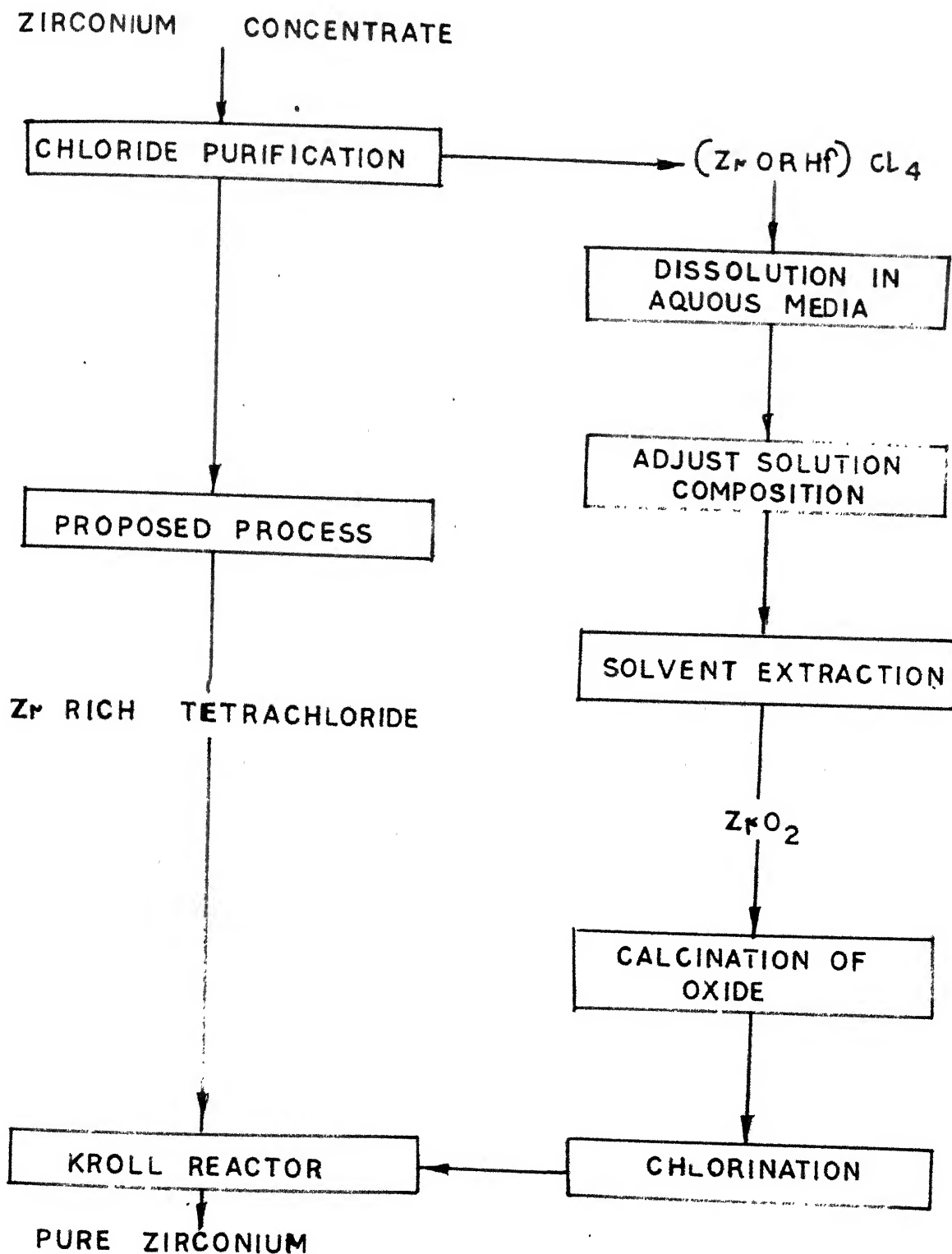
FIG I FLOW DIAGRAM FOR EXTRACTION OF ZIRCONIUM & HAFNIUM

ting solution is adjusted with large amounts of nitric acid, thiocynic acid, amonium thiocynate and so forth in prepation for the solvent extraction process. During the solvent extraction process the aquous Zr (Hf) bearing concentrate is repeatedly contracted with an organic phase such as tributyl phosphate in kerosene or methyl isobutyl ketone (hexone) to effect the seperation of the two elements. For either solvent extraction process, the Hafnium free Zirconium undergoes various precipitation-dissolution steps until it is finally obtained as hydrous zirconiumoxide precipitate which is calcined and subsequently chlorinated to produce the zirconium tetrachloride feed for the kroll reactor. .

A chemical method proposed schematically for the seperation of Zirconium- Hafnium, is based on the principle of the differences in the chemical stabilities of the complexes formed between solid or liquid halides and $Zr(Hf)Cl_4$. Because Hafnium complexes are more stable than the corresponding zirconium compounds, more volatile Zirconium tetrachloride is removed with the vapour phase preferentially during distillation.

1.2 Chloro-hafnates and zirconates of alkali metals

Hexachlorocompounds of zirconium and hafnium of the general chemical formula $M_2 X Cl_6$, where M stands for alkali metals (Zi to Cs) and X stands for zirconium and hafnium, have been identified in several phase diagrams studies of systems, of the type $MCl- XCl_4^{2-8}$. Reactions leading to the formation of double salts of alkali metals may be written as :-

$$2MCl + XCl_4$$

$$2MCl + XCl_4 \cdot Mc2MCl \cdot XCl_6 XCl_4 = M_2XCl_6 \qquad (1)$$
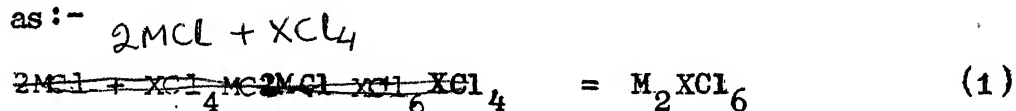
The systems $NaCl-HfCl_4$, $KCl - Zr Cl_4$, $KCl-HfCl_4$, $CsCl- ZrCl_4$ and $CsCl- HfCl_4$ were studied by Morozov and Sun- In-Chuzhu[3] in almost the entire composition range. These systems showed several common characteristics. In all the cases, two eutectics and a congruently melting compound M_2XCl_6 obtained. . A list of the important features of this class of systems is given in Table II. Only those systems for which informations are available in the entire composition range are included in the table.

The $MCl- M_2XCl_6$ portion of such phase diagrams, in particular, have received considerable attention in the recent past because of the technological importance of the compounds, M_2XCl_6. This region of the phase diagram is

TABLE II — IMPORTANT FEATURES OF SYSTEM MCl – XCl$_4$

System	Eutectic 1		Eutectic 2		Congruently melting compound M$_2$XCl$_6$ (all at 66.7 mole percent)		Other compounds		
	Melting point °C	Mole Percent MCl	Melting Point °C	Mole Percent MCl	Melting point °C	Polymorphic transformation °C	Compound	Melting point °C	Mole percent MCl
MaCl$_4$–ZrCl$_4$	548	72.0	314	37.6	646	–	Na$_2$ZrCl$_5$ Na$_2$Zr$_2$Cl$_9$	381 317	50.0 33.3
NaCl–ZrCl$_4$	539	76.0	311	38.0	695	α – β β – γ	–	–	–
NaCl–ZrCl$_4$	525±5	71.5	312±5	37.0	626±5	β – α ≈ 382	Na$_3$ZrCl$_7$	535±5	72.0
NaCl–HfCl$_4$	540	73.4	330	40.6	660	α–β 384 β–γ 440 γ–δ 484	–	–	–
KCl–ZrCl$_4$	594	75.8	220	42.2	798	–	–	–	–
KCl–ZrCl$_4$	600±5	77.0	225±4	35.0	790±5	–	K$_7$Zr$_6$Cl$_{11}$	565±5	52.0
KCl–HfCl$_4$	604	77.6	242	38.0	802	α transformation at 550 °C	–	–	–
CsCl–ZrCl$_4$	572	84.8	286	22.8	805	–	–	–	–
CsCl–HfCl	590	81.6	302	34.9	820	–	–	–	–

is characterised by phases with relatively low vapour pressu-res. The system therefore provides for a suitable electrolyte for electrolytic extraction of zirconium and hafnium metal[2].

The hexachloro compounds are also of interest from the point of view of seperation of zirconium from hafnium. A suitable technique for seperation may be developed based on the differe-nce in the thermal stabilities of the hafnium and zirconium compounds. The thermal stability, which is characterised by the equilibrium vapour pressure of tetrachloride over these compounds was first investigated by Morozov and co-worker[11]. The vapour pressure data indicated increasing stabilities with increase in the ionic radii of cations of the reacting metal cholorides . The order of stabilities was found to be :

$Cs_2ZrCl_6 \rangle K_2ZrCl_6 \rangle Na_2ZrCl_6$. The same order prevailed for haf-nium compounds also. Durtrizac and Flangas[2] confirmed these findings later.

1.3 General description of alkali chloride – $Zr(Hf)Cl_4$ system

Since the proposed scheme involved alkali chloride – $Zr(Hf)Cl_4$ systems a discussion of some relevant information reported in the literature would be appropriate.

Luthra, Majundar, Bhat & Reddy [10-18] investigated

these systems to evolve a new process for seperating

hafnium from zirconium. The proposed method envisaged

reaction between gaseous mixture containing $ZrCl_4$ and $HfCl_4$

and solid sodium chloride or pottassium chloride in a packed

bed flow reactor. It was found that preferential formation

of sodium hexachlorohafnate led to enrichment of gaseous

phase with zirconium tetrachloride. Mazundar[1] studied the

effects of various parameters e.g. temperature, flow rate,

particle size and bed length. The seperation efficiency

$\in$, which is defined as

$$\in = \frac{Wt. - \% \text{ zirconium in output}/Wt.-\%Hf \text{ in}O/\text{p}^{\text{output}}}{Wt.- \% \text{ Zirconium in I/P }/Wt.-\% \text{ Hf in}I/P \text{ input}}$$

was found to have increased by an increase in bed length

and by decrease in particle size and flow rate of the gas.

Temperature does not affect the seperation appreciably.

Seperation coefficients higher than thermodynamically

possible were acheived in a number of runs.

Kinetics of the reaction of vapours of $ZrCl_4$ and

$HfCl_4$ together as a mixture and seperately with solid

spheres of NaCl voere investigated by Majumdar [11-13] using

gravimetry methods. This was done by measuring the weight

changes of sodium chloride spheres using caliberated quartz

springs. Formulation of reaction mechanism was augmented by

conducting inert marker experiments. The rate of formation of

compounds e.g. Na_2ZrCl_6 and Na_2HfCl_6 , were studied as a

function of tetrachloride pressure, temperature and particle

size. Under similar conditions the reaction with $HfCl_4$ was

invariably found to be slower. The data obtained in kinetic

studies was tested against various heterogenous solid-gas

kinetic models. Of these models Carter-Valensi model, which

is diffusion in the product phase controlled gave a consisten-

tly good fit. The possible reaction mechanisms have been

postulated in the light of pressure and temperature dependence

of the specific rate constant and the marker experiments. On

the basis of the experimental evidence, the transport of the

chlorine ions from the unreacted core towards the outer

product-gas interface appeared to be the most likely reaction

mechanisms. It was presumed that material transport occurred by

vacancy mechanism. Both hexachlorohafnate and zirconate conformed

to the same reaction mechanism within the experimental range.

However, with the change in polymorphic form of the

reaction product it was suggested that the reaction

mechanism also changed.

Some preliminary investigations[16] on simultaneous

formation of hexachloro compounds were also carried out

by heating sodium chloride spheres with vapour mixture of

zirconium tetrachloride and hafnium tetrachloride. In these

experiments, additional investigations were performed to

ascertain the partial pressure of reacting gas mixture and

the composition of the gas phase. Total pressures were

determined by seperate experiments.

Roy[17], Bhat[10], and Reddy[18] designed and fabricated

an apparatus for kinetic studies by transpiration technique.

They had investigated the kinetics of the reaction $ZrCl_4$

vapours with particles of NaCl, KCl, and mixtures of these.

It was shown that the reaction with pure KCl was faster

than that with pure NaCl.

Vapour pressure measurements over $ZrCl_4$, $HfCl_4$,

Na_2ZrCl_6 and Na_2HfCl_6 compounds was carried out by Bhat[10]

also made theoretical calculation for fractional deconpo-
sition and sublination of compound $Na_2 ZrCl_6$. The calcu-
lations were done for different gas flow rates,different
initial conpositions of the vapour and for different final
conpositions of the vapour. It was shown that
increase in solid flow rate and decrease in gas flow rate
decreases the number of plates necessary to achieve any
predetermined seperation.

Reddy[10] further extended the measurements and
determined the relative stabilities of hexachlorocompounds
of Potassium, Rubudium & Cesium. Reliability of consistant
pressure measurements was obtained by using the tin isoteni-
scope. However same pressure data for some compounds differs
significantly from those available in the literature. But it
was generally proved the zirconates for alkali metals were
more stable than the corrosponding hafnates.

Kinetic studies conducted involving flow of tetrachlo-
ride gas ($ZrCl_4$) through packed beds indicated that initial
stages of the conpound formation reaction may be understood
in terms of Jander's[19]. Model for gas solid reaction.

Comparitively smaller values of rate constant as obtained

from the data, indicated that the mechanism of the

reaction in the initial stages may be different from that

prevalent in the later stages. The rate constant values

however indicated that any scheme based on fractional

sublimation of hexachloro hafnate zirconate mixture must

make provisions for increasing the reaction rates by using

higher pressure and temperatures, smaller particle sizes,etc.

1.4   Aim of the present work

The aim of the present investigations was

twofold. Firstly it was to substantiate data on the reaction

of $ZrCl_4$ vapours with a bed of sodium chloride particles as

a function of time pressure and temperature. The study aimed

at collecting sufficient relevant data to establish the rate

and the model of reaction mechanism under various experiment-

al conditions for use in the operation of a reactor designed

for use in Zr- Hf seperation. The second aim was to actually

fabricate the reactor whose basic design was finalised by

Reddy. Regarding the first aim, particular emphasis was

laid on reestablishing the rate of reaction of $ZrCl_4$ with a

packed bed of NaCl & KCl particles as a function of the
composition of the bed. Compositions at which unusually high
reaction rates could be obtained were to be established
clearly.

The present report comprises of six chapters. After
this chapter the next chapter 2 deals with theoretical consi-
derations regarding the heterogenous gas- solid reactions and
deals with mainly the kinetic aspects of the reaction of
zirconium tetrachloride with alkali chlorides. This is then
followed by the chapter on experimental procedures. Chapter 4
gives the results and discussions. Chapter 5 gives, an engi-
neering description of the reactor for the fractional subli-
mation of $ZrCl_4$, designed and fabricated in this laboratory.
Chapter 6 summarises the main conclusions of the present
investigations and lists some suggestions for future work.
The thesis is concluded by a list of references.

CHAPTER -TWO

GENERAL

Non catalytic gas solid reactions are of considerable industrial importance and are widely utilized in chemical and metallurgical industries. Examples are reduction of oxides, reduction of metal halides (Kroll's process), oxidation of metals,gasification of coal,etc.The reactions can be classified according to the phases in which the various species occurs or by the mode of the reaction. They are also classified according to the nature of the product whether its a poreus or non porous.

2.1 The alkali hexachlorozirconates and hafnates

Under suitable conditions both zirconium and hafnium tetrachloride react with each alkali chloride e.g. NaCl, KCl, RbCl or CsCl to form hexachlorocompounds of the type M_2XCl_6 where M represents alkali cation and X either zirconium or hafnium. In general the hexachlorocompounds represent highly stable forms of reactive tetrachlorides.

When a mixture of the tetrachlorides of zirconium and hafnium in the vapour state is passed through heated NaCl (or any other alkali chloride)the vapour becomes richer in zirconium as the reaction proceeds. Consequently

the solid phase exhibits a higher hafnium content when comp-
ared to the orginal vapour.Zirconium and hafnium tetrachlorides
react with alkali chlorides according to the following:-

$$2NaCl \quad + \quad ZrCl_4 \quad = \quad Na_2ZrCl_6$$
$$2NaCl \quad + \quad HfCl_4 \quad = \quad Na_2HfCl_6$$
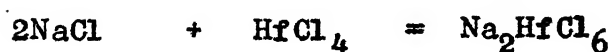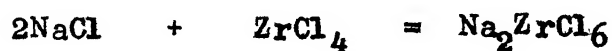
The compounds form ideal solid solution. While the te-
trachlorides are highly volatile, the hexachlorocompounds
exhibits much lower pressures.Thus these compounds may be
looked upon as stable forms of the tetrachlorides. In recent
years several investigations have been reported concerning
the stabilities of these compounds, the kinetics of their
formation, the phase diagrams and the physical properties.
The hexachlorocompounds are of interest in fused salt extra-
ction in view of their stabilities which are further enhan-
ced by dissolving them in alkali chlorides. But such solu-
tions are not always thermally stable and losses of the
volatile tetrachlorides through distillation may present
problems. Also the deposits obtained are usually dendritic
or a loosely adherent metallic powder. Flengas and Pint[20]
have investigated various factors in selecting a potential
fused salt media for zirconium and Hafnium extraction and
have studied the stability of some of the hexachlorocomp-
ounds of zirconium and hafnium. According to them,solutions
of these compounds in alkali chloride melts are suitable for
use
in open electrolytic cells under inert atmosphere.

The $MCl- M_2ZrCl_6$ and $MCl- M_2HfCl_6$ are related by simple eutecti● type of phase diagrams which clearly indicate the stability of the congruently melting chloro complexes. Thus at a given temperature, a decomposition equilibrium

$$M_2XCl_6 = 2MCl + XCl_4 \qquad (1)$$

$$\text{(s, l, or sol.)} \quad \text{(s, l, or sol.)}$$
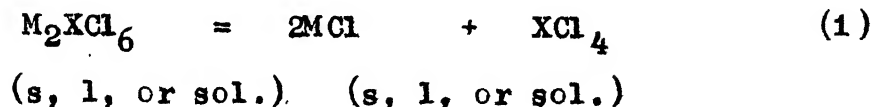
establishes higher equilibrium pressures of $ZrCl_4$ over the tetrachlorozirconates than that of $HfCl_4$ over the tetrachlorohafnates. It is thus possible to achieve a thermodynamic seperation of zirconium and hafnium.

A typical phase diagram for the system $MCl-XCl_4$ is shown in the figure 2a. The compound rich side of the subsystem $MCl- M_2XCl_6$ is of special interest here. The correspondence between the pressure temperature plots and $MCl- M_2XCl_6$ phase diagrame is obtained from the following considerations.

The equibibrium vapour pressure of the tetrachloride is determined by the decomposition reaction for which the equilibrium constant is

$$K = \frac{a^2_{MCl} \ X \ P_{XCl_4}}{(\ a_{M_2XCl_6}\ )}$$

Where 'a' is the activity with respect to the pure solid at
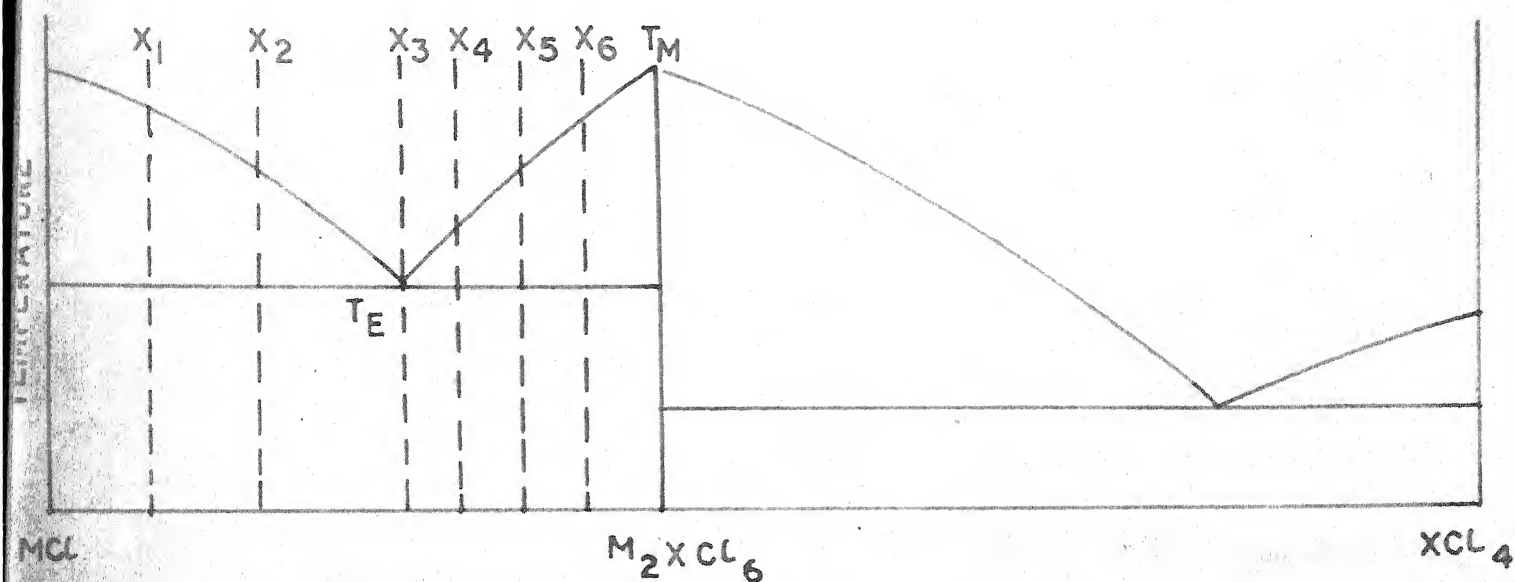
FIG 2a PHASE DIAGRAM FOR SYSTEM MCL—XCL₄
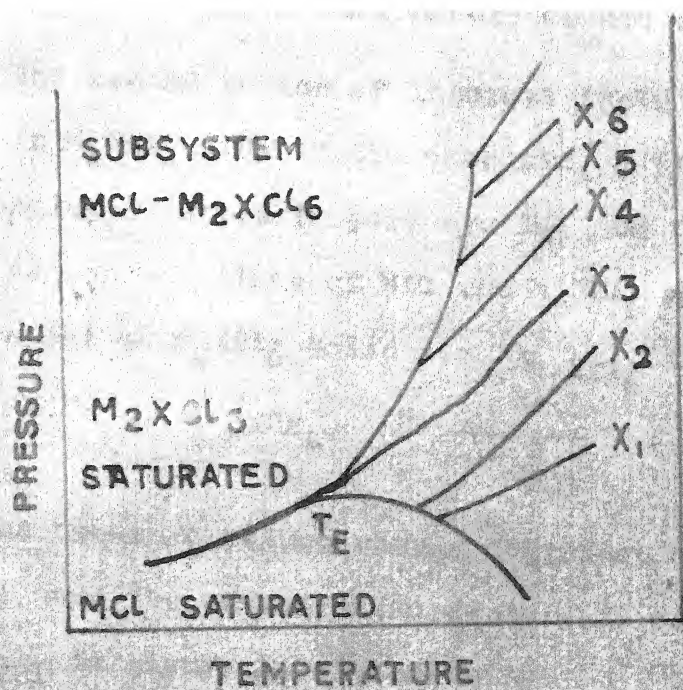
FIG 2b THEORETICAL PRESSURE VERSUS TEMPERTURE CURVES FOR A SYSTEM HAVING ONE REACTIVE COMPONENT

the standard state and 'P' the partial pressure of the tetra-
chloride in the gas phase.

Since there is no solid solubility, the equilibrium
constants equals the partial pressure below the eutectic
temperature and is given by the Vant Hoff relationship

$$d \ln P_{XCl_4} / d (1/T) = -\Delta H_R^o / R \qquad (3)$$

where ΔH_R^o is the standard heat of reaction (assumed
constant over a limited range), the plot of log P_{XCl_4}
versus reciprocal of temperature would be linear. The pre-
ssure values are also independent of the composition of
$MCl - M_2XCl_6$ mixture in this temperature range because
the pressure over the alkali chlorides are negligible.

The second region of interest includes all compo-
sitions in M_2XCl_6 side of the eutectic, defined by the
corresponding eutectic temperature T_E, and the liquidus line.
In this region solutions of MCl and M_2XCl_6 and
with respect to M_2XCl_6 solid i.e. $a_{M_2XCl_6}$ is always unity,
therefore $\qquad P_{XCl_4} = \dfrac{K'}{a_{MCl}^2} \qquad (4)$

The pressure values should therefore increase more
rapidly, once the eutectic temperature is exceeded because
their a_{MCl} is always less than unity

For all the solutions just above the eutectic tempe-

rature, a_{MCl} has common value, namely, the activity of MCl in the $MCl - M_2XCl_6$ eutectic composition. As the temperature is increased a_{MCl} changes along the liquidus line. The trend is again common for all compositions upto the liquidus temperature. Thus for all compositions in the subsystem $MCl - M_2XCl_6$, the pressure - temperature plot has a common trend upto the liquidus line.

Beyond this liquidus temperature the system at any composition is described by an homogenous solution of $MCl - M_2XCl_6$ and by XCl_4 vapour. The equilibrium vapour pressure of the tetrachloride is now given by

$$P_{XCl_4} = \frac{K \, a_{M_2XCl_6}}{a^2_{MCl}} \qquad (5)$$

The pressure curve will undergo a decrease of slope because of the introduction of $a_{M_2XCl_6}$ term. More over P_{XCl_4} will now vary with temperature mostly due to the variation of K. The pressure temperature curve would be again linear over small temperature ranges above the liquidus.

Differentiating the free energy equation with respect to temperature and combining it with Gibbs - Helmholty it is seen that

$$\frac{d \ln P_{XCl_4}}{d \, (1/T)} = \Delta H^{\circ}_R \, \frac{-(\Delta H^{\circ}_{M_2XCl_6} + 2 \Delta H_{MCl})}{R}$$

Therefore the plot of log XCl_4 versus $(1/T)^{\circ}$ K is again

linear over a limited temperature range provided the terms within brackets on the right hand side are small compared to ΔH°_R , otherwise the line would be curved.

Considering the compositions in the MCl saturated side of the eutectic at $T_L \rangle T \rangle T_{E_1}$, where T_L is the liquidus temperature, the phases present are pure solid. MCl in equilibrium with a solution of M_2XCl_6, MCl and XCl_4 vapour. In this range

$$a_{MCl} = 1$$

and $\qquad P_{XCl_4} = a_{M_2XCl_6}$

For a given mixture, increasing the temperature to that above the eutectic would cause a decrease in slope of the pressure curve. The predicted shape of the common pressure curve representing the liquidus line for the phase diagram is given in the figure 2 (b) . The pressure for liquidus line for MCl decreases as the solution become more dilute in M_2XCl_6 and eventually reaches zero at the melting point of pure MCl.

For temperature higher than the liquidus temperatures, equation (5) again becomes applicable and the pressure curves for various compositions slope upwards at the corrospending liquidus temperature as shown in curves 1,2,3 in the figure 2 (b).

The available information on the phase diagrams in these systems is summarised in figure 3. The pressures over some compounds have been shown by Bhat[10], to be given by the following equations:

Compound	Equation	Temperature $^\circ K$
$ZrCl_4$	: log P $_{ZrCl_4}$ (torr) $= -\dfrac{2553.6}{T}$ +6.80	(210-382)
$HfCl_4$	: log P $_{HfCl_4}$ (torr) $= -\dfrac{5116.4}{T}$ +11.57	(190-323)
Na_2ZrCl_6	: log P $_{Na_2ZrCl_6}$ (-do-) $= -\dfrac{7965.9}{T}$ +11.51	(439-646)
Na_2HfCl_6	: log P $_{Na_2HfCl_6}$ (-do-) $= -\dfrac{6188.7}{T}$ + 9.11	(45-660)

2.2 Kinetic studies on Zr (or Hf)Cl$_4$ - NaCl system using single crystals

The kinetics of hexachlorocompound formation is dependent upon a number of factors viz. the tetrachloride gas pressure, temperature, nature of the salt, time of reaction etc. Dutrizac[21] studied the kinetics of hexachlorocompound formation by the reaction of the tetrachloride gas at a given pressure with a single crystal of the salt at a given temperature.

The method consisted of measuring the weight gain in the single crystal of the salt when reacted with the tetrachloride vapours. A schematic diagram of the apparatus used is given in fig. 4.Weight gain measurements were done

776

TEMP °C

KCL   22·4 (MOLE%) K_2HfCl_6

K_2HfCl_6

98

694

77½

TEMP °C

KCL   24·2 (MOLE%) K_2ZrCl_6

K_2ZrCl_6 ⟶

TEMP °C

CsCL   18·4 (MOLE%) Cs_2HfCl_6

Cs_2HfCl_6

817

588·4

646

TEMP °C

CsCL   15·2 (MOLE%) Cs_2ZrCl_6

Cs_2ZrCl_6 ⟶
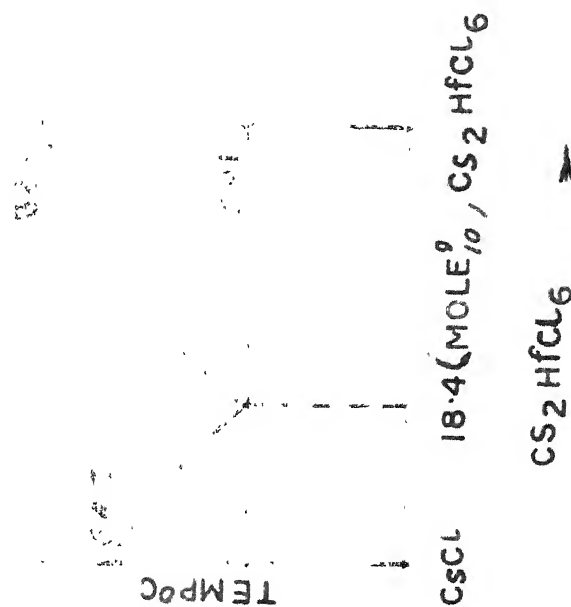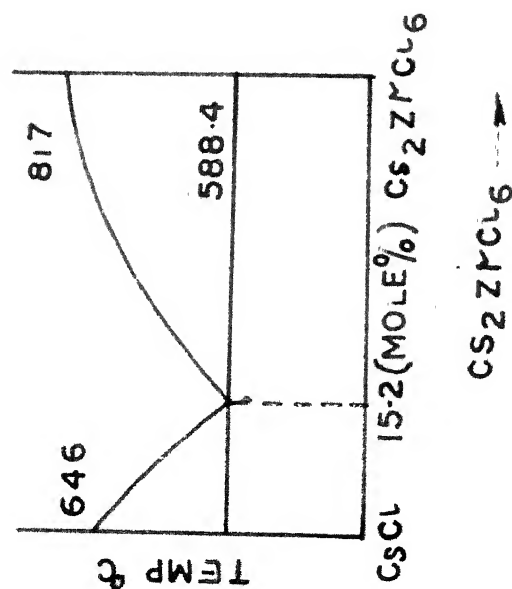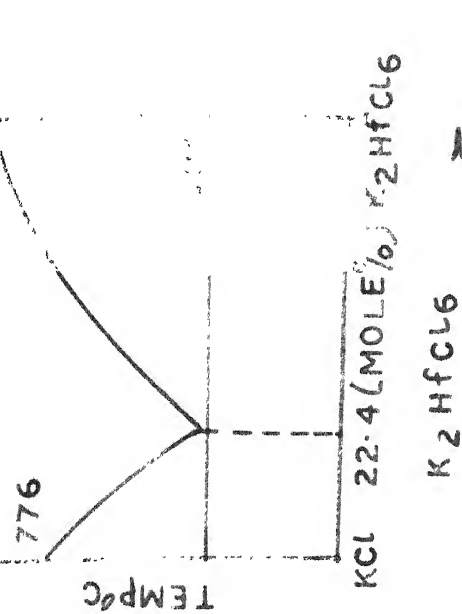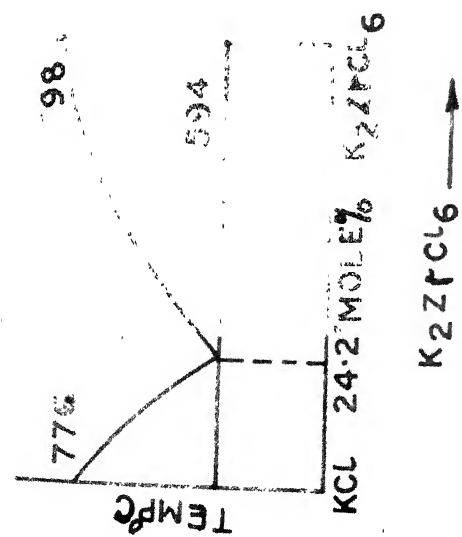
FIG 3   SCHEMATIC PHASE DIAGRAMS

(FROM THE LITERATURE 15, 20)

at stipulated intervals of time using a quarts spring from
which the single crystal was hung by means of a fine platinum
wire. The tetrachloride pressure in the system was kept
constant by carefully maintaining the temperature of the
bulb containing the tetrachloride. Similarily the temperature
of the single crystal was maintained constant at any desired
temperature. Condensation of the tetrachloride in the system
was avoided by heating arrangements at proper places. Before
producing tetrachloride vapours it was absolutely necessary
to evacuate the entire system otherwise the results could be
misleading. Before the start of the experiment room temperature
calibration of quartz spring was done in the following manner.

Suitable weights were attached to the quartz spring
balance and the change in total length of the spring was
measured by a cathetometer. The spring constant was then
determined. The room temperature spring constant had to be
converted to the appropriate high temperature value using
standard spring theory.

Spring constant x K (gm/cm) = $K'G$ (7)

where K' is approximately constant for quartz and G is
the shear modulus of the spring material which is tempera-
ture dependent. This simple equation with Horton's values
for the shear modulus of a function of temperature was then
used to calculate the high temperature for spring constant.
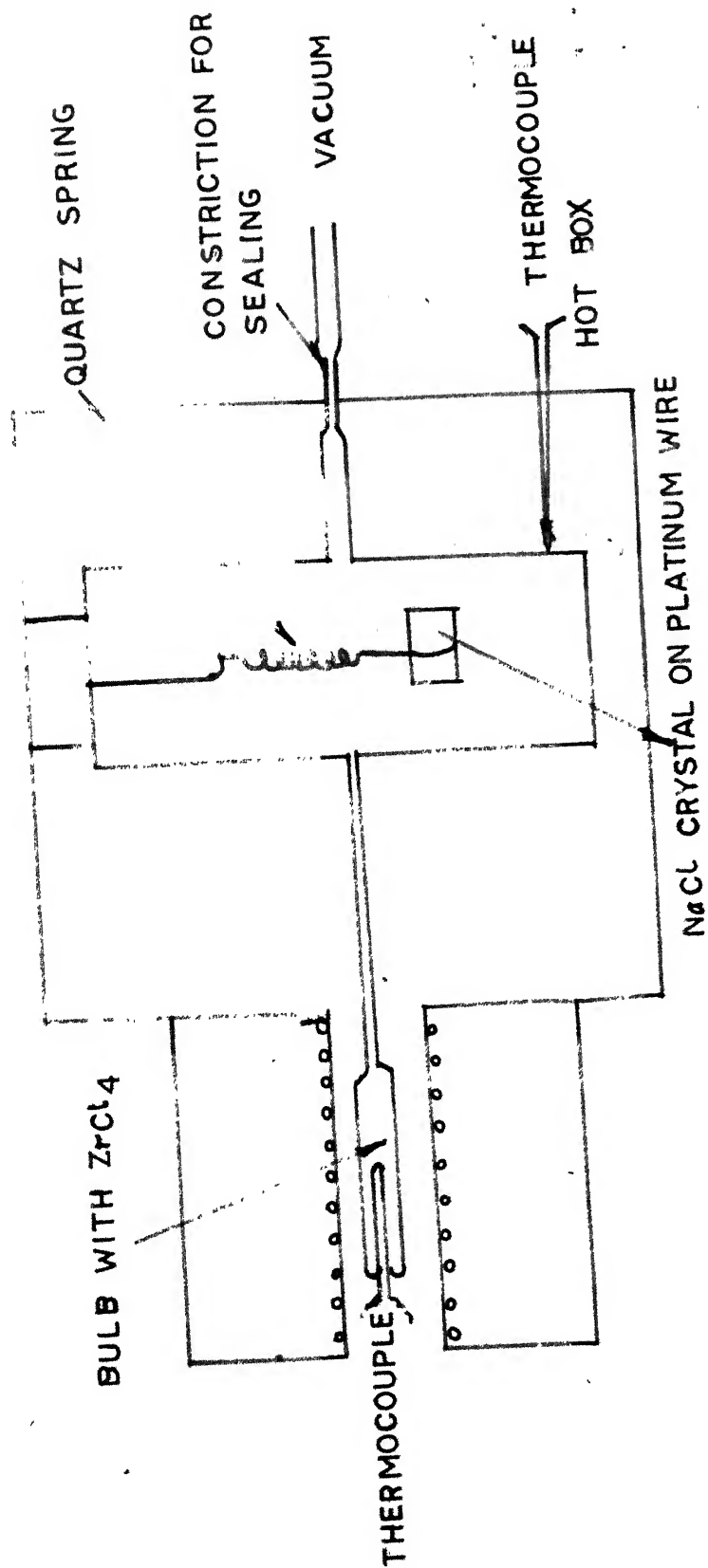
FIG 4 APPARATUS FOR KINETIC INVESTIGATIONS

Labels within the figure:

QUARTZ SPRING

CONSTRICTION FOR SEALING

VACUUM

THERMOCOUPLE

HOT BOX

NaCl CRYSTAL ON PLATINUM WIRE

BULB WITH ZrCl₄

THERMOCOUPLE

21

Experiments with single crystals of sodium chloride with zirconium tetrachloride yielded certain interesting results. There was a parabolic relationship between weight gain and time of reaction suggesting that the kinetics of the hexachlorocompound formation is diffusion controlled. Increases in the temperature and the pressure of tetrachloride resulted in increased weight gain for a given time of reaction. This has commercial significance in the preparation of hexachlorozirconate or the chlorohafnates. Also, since the reaction is found to be diffusion controlled, finer particles of sodium chloride and higher gas pressures should favour faster chlorozirconate and chlorohafnate fomation.

2.3 Kinetic studies on $Zr(orHf)Cl_4$- NaCl system using single spheres.

Mazundar[16] has studied the kinetics of formation of double compounds, Na_2ZrCl_6 using the principle of thermogravimetry in an all glass closed apparatus. A schematic diagram of the apparatus is given in figure 5. The set up consisted of a vertical reaction chamber connected to a gas generating bulb containing solid tetrachloride ($ZrCl_4$, $HfCl_4$, or mixture of the two). The sodium chloride sphere w $\approx$ suspended from a calibrated quartz suspension spring into the constant temperature zone of the reaction chamber. A seperately heated connecting tube led the vapours from a

6

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1. TROLLEY FURNACE
2. ALUMINIUM BLOCK
3. BULB CONTAINING TETRACHLORIDE
4. MEASURING THERMOCOUPLE
5. CONTROLLING THERMOCOUPLE
6. SPRING HEATER
7. QUARTZ SPRING
8. QUARTZ BASKET
9. SODIUM CHLORIDE BALL
10. REACTION FURNACE
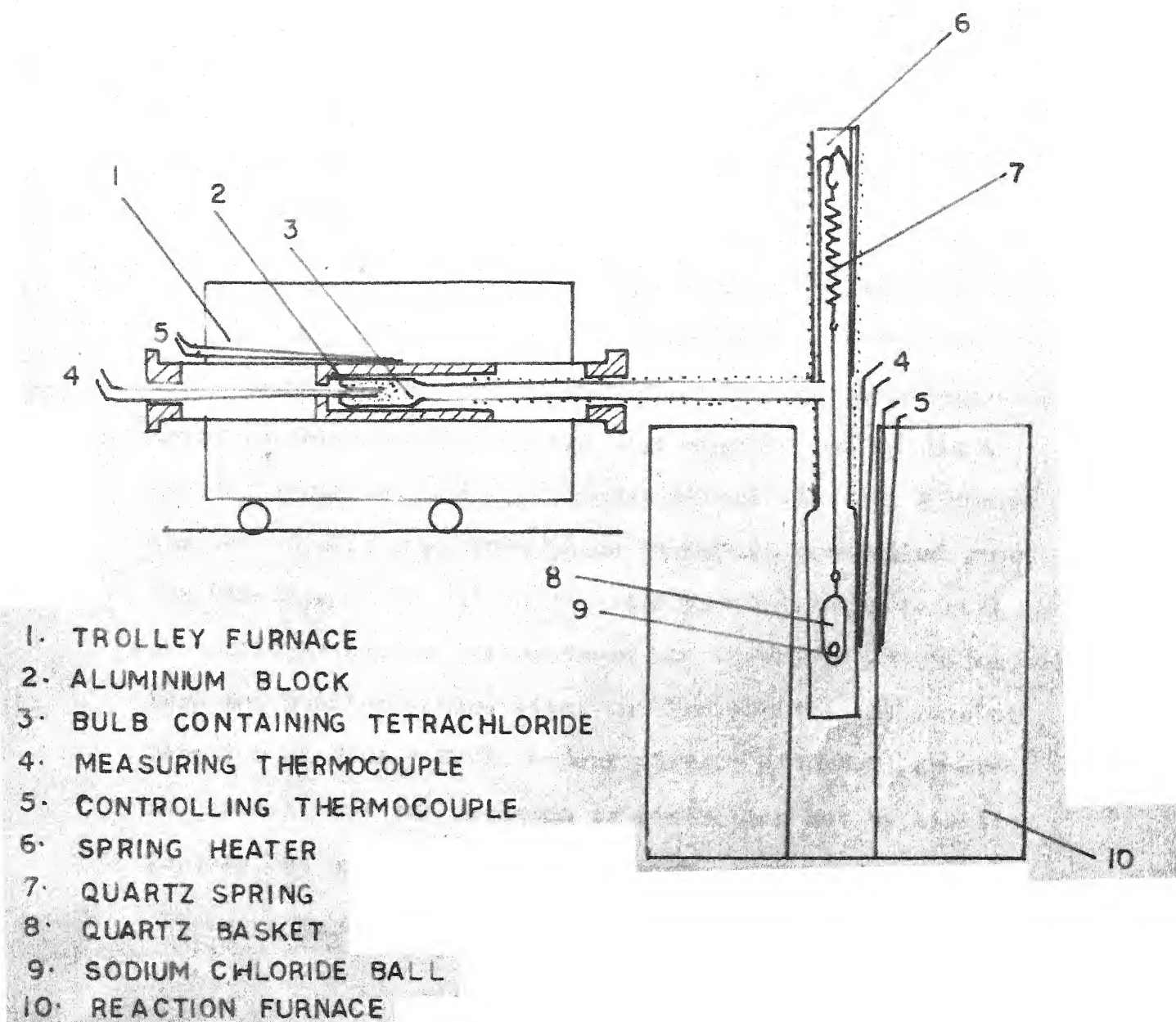
FIG 5   APPARATUS FOR KINETIC STUDIES[16]

heated bulb into the reaction chamber at a constant tempera-
ture. Other heating arrangements were provided at proper
places in the apparatus so that there was no condensation
of the tetrachloride vapours. All weight gain measurements
were obtained using a quartz spring. Weight change was
recorded by measuring the change in spring length viewed
through a narrow slit in the refractory casing that surroun-
ded the spring region of the apparatus.

Mazundar's apparatus was designed to study the effect
of parameters such as reaction temperature, gas pressure and
sphere size on the rate of formation of hexachlorocompounds.
Inert marker experiments were also carried out to aid the
kinetic analysis. His experiments showed that the kinetics
was essentially a product phase transport controlled process.
The kinetics of formation reaction were found to be more
favourable at higher gas pressure and higher reaction tempera-
ture and smaller sphere size. He also studied the rate of
reaction of $HfCl_4 - ZrCl_4$ vapour mixture with $NaCl$ spheres
and showed that the reaction is controlled not by kinetic
factors but by the exchange reaction

$$Na_2ZrCl_6 + HfCl_4 = Na_2HfCl_6 + ZrCl_4 \quad (8)$$
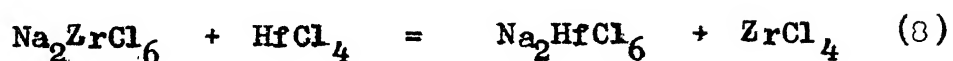
2.4 Reactions involving Non-porous product

Solid gas reaction models essentially are rate equations expressed in terms of parameters which characterize one or more of the reaction steps viz.chemical reaction at the interface, transport through the solid reaction product and the surrounding gas phase. The reactions may be under single or multi step control. The manner in which reaction steps can be synthesized for building a representative model primarily depends on the nature of both the product and the reactant solid i.e. the extent of porosity. Figure 6 depicts the various situations that can be encountered. A sharp interface may result for both porous and non-porous product layer, figure 6 (a) . In this case the reaction steps leading to the product formation occur in series.

Diffused reaction interface figure 6 (b), is often contended as the most general manner in which heterogenous solid-gas reaction can take place. It has been argued that for porous reatant and product, and under the condition of mixed control, the reacting gas may diffuse past partially reacted solid particles. In other words, reaction may occur in diffused zone, where concentration gradient occurs both in the solid and the gas phase.

The third possibility is occurance of the reaction in virtually homogenous manner. If the porosity of the reactant
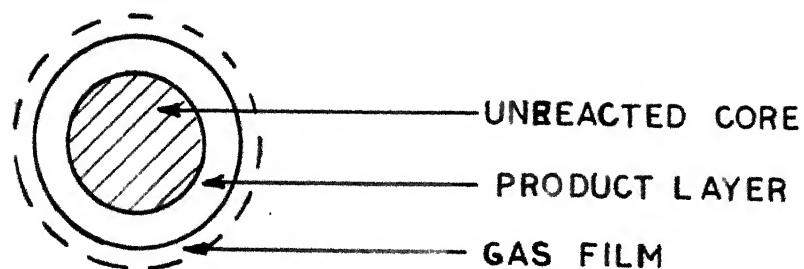
(a) SHARP INTERFACE (POROUS & NONPORUS PRODUCT BOTH)

- UNREACTED CORE
- PRODUCT LAYER
- GAS FILM
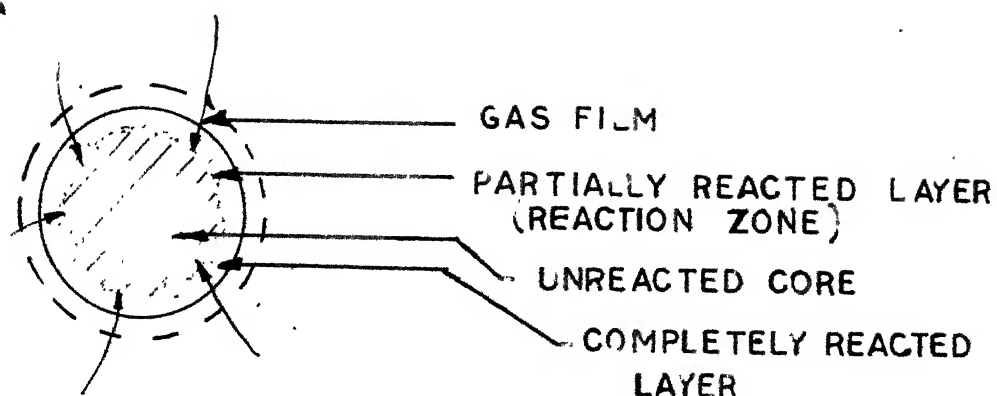
(b) DIFFUSED INTERFACE (POROUS PRODUCT ONLY)

- GAS FILM
- PARTIALLY REACTED LAYER (REACTION ZONE)
- UNREACTED CORE
- COMPLETELY REACTED LAYER
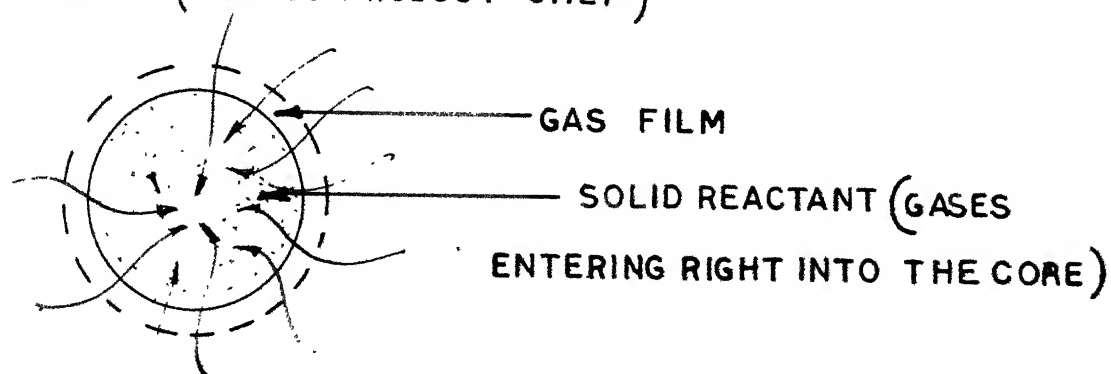
(c) HOMOGENEOUS REACTION (POROUS PRODUCT ONLY)

- GAS FILM
- SOLID REACTANT (GASES ENTERING RIGHT INTO THE CORE)

FIG 6 SCHEMATIC REPRESENTATION OF DIFFERENT SOLID GAS REACTIONS

solid is very high, the reactant gas may permeate right into
the central core. Under such circumstances the reaction takes
place in the entire solid simultaneously and a concept of a
reaction interface virtually disappear as in figure 6 (c).

A large number of reaction models have been proposed
to quantitatively, explain the kinetics of all the three
classes of reactions. If the reaction product is non-porous,
the resistance by the boundary layer may be neglected as
compared with the solid product layer. If diffusion through
the product is the rate limiting step and the reaction inter-
face is plane, then the rate of chemical reaction i.e. the
rate of thickening of the product layer is inversely propor-
tional to the thickness

$$\frac{dy}{dt} = \frac{K'}{y} \qquad (9)$$

where K' is the reaction rate constant and y is the thick-
ness of the product layer. Integration gives

$$y^2 = 2K't \qquad (10)$$

This is the well known parabolic law. If the
solid is in the form of a sphere the above parabolic law
will not hold because the surface area for the reaction
changes continuousl y during the reaction. A number of
solutions have been proposed for spherical particles;
Jander's approximate equation, a simplified equation due
to Crank Ginstling and Brounhstein and Carter Valensi's
exact solution.

Jander's solution [19]

Jander developed an approximate solution by using the equation of the parabolic law. If r_0 is the initial radius of the particles and ρ_r is the density of the reactant, then the fraction reacted, F, will be given by

$$F = \frac{4/3\pi r_0^3 \rho_r - 4/3\pi(r_0 - y)^3 \rho_r}{4/3\pi r_0^3 \rho_r} \qquad (11)$$

$$= \frac{1-(r_0 - y)^3}{r_0^3}$$

so

$$y = r_0 \left[1 - (1 - F)^{1/3} \right] \qquad (12)$$

By substituting the value of y into the parabolic law equation we get

$$\left[1 - (1 - F)^{1/3} \right]^2 = K_j \cdot t \qquad (13)$$

where t is time in hours.

The limitations for this model are that the equation is correct only if the volume of the unreacted core plus the volume of reaction product equals the volume of orginal material. This holds approximately at the initial stages of reaction.

Crank-Ginstling and Brounstein simplified model [27-28]

These researchers developed a rate equation by taking a simplifying assumption that the volume change of the sample with time is zero.

The equation is

$$\frac{2M_r DC}{\alpha_1 \int r_o^2} \quad = \quad 1 - 2/3\ F - (\ 1 - F\ )^{2/3} \qquad (14)$$

or $\qquad K_{GB} \cdot t \qquad = \quad 1 - 2/3\ F - (\ 1 - F\ )^{2/3} \qquad (15)$

where M_r is the molecular weight of reactant, D is the diffusion coefficient, C is the concentration of the reagent and α_1 is the stoichiometry factor.

This equation has been found to give better agreement than Jander's equation but still it fails at higher percentages of reaction because it does not take into account the change in volume of the sample with time.

Carter Valensi's exact solution [29-32]

The exact rate equation was developed independently by the Carter and Valensi. The equation is simplified to,

$$\left[1 + (\ Z - 1\ )\ F\right]^{2/3} + (\ Z - 1\ )\ (\ 1 - F\ )^{2/3} = K_{CV} \cdot t \qquad (16)$$

where Z is the swelling parameter and K_{CV} is the reaction rate constant. This equation has been found to hold upto 100 percent of the reaction.

CHAPTER -THREE

EXPERIMENTAL

3.1 General

The $ZrCl_4(g)$, $HfCl_4(g)$ - NaCl system presents several experimental difficulties. Some of these are as follows

(i) The vapour pressures over these compounds ($HfCl_4$ and $ZrCl_4$) are often very high. This precludes the use of open cell and necessiates the employment of isolated vessels which must be heated sufficiently to prevent condensation of the gas in the apparatus. The temperature in the complete system should be higher than the temperature of the bulb containing $ZrCl_4(s)$ or $HfCl_4(s)$. If at any point the temperature drops down below the bulb temperature, condensation will occur and a pressure lower than in equilibrium with $ZrCl_4(s)$ in the bulb will be established in the system.

(ii) All chlorocompounds of zirconium and hafnium are very hygroseopic and absorbed water cannot be removed without effecting compositional changes in the salts. Further, these compounds have high affinity for oxygen. Thus, all the handling operations must be carried out in a dry box fitted with dry inert gas.

(iii) These chlorides are highly corrosive in nature.

This fact together with high reactivity of $ZrCl_4$ and $HfCl_4$ vapours towards oxygen and moisture precludes the use of general corrosive materials.

(iv)   The alkali halides are very hygroscopic. Unless the moisture is completely removed from alkali halide sample, the vapour ($ZrCl_4$) may react with it to form a coating of oxychloride which may hamper the reaction rate. This requires a prolonged heating of the halides in the vacuum to remove moisture. Certain alkali halides are so hygroscopic that the moisture cannot be removed by heating without compositional changes.

3.2 Transpiration technique

This technique essentially consisted of passing the vapours of the tetrachloride over the alkali chloride particles with the help of a carrier gas. Essentially it allows for the reaction between the tetrachloride vapours and the alkali chloride without allowing any condensation of the tetrachloride over the alkali chloride. A schematic diagram of the apparatus is given in the figure 7. The technique as practised in the laboratory has certain special features with respect to the apparatus used.

1. There is provision for purifying the carrier gas by use of associated gas train.

2. The temperature of the system can be adjusted so

TO MCLEOD GAUGE

VACUUM

STOP COCK

BUBBLER

COPPER FURNACE

TITANIUM FURNACE

FLOW METER

BUBBLER

TUBE CONTAING ALKALI CHLORODE

BULB CONTAING TETRACHLORIDE

THERMOCOUPLE

GENERATING FURNACE

REACTION FURNACE

CONDENSATION COLUMN

CLEANING UNIT
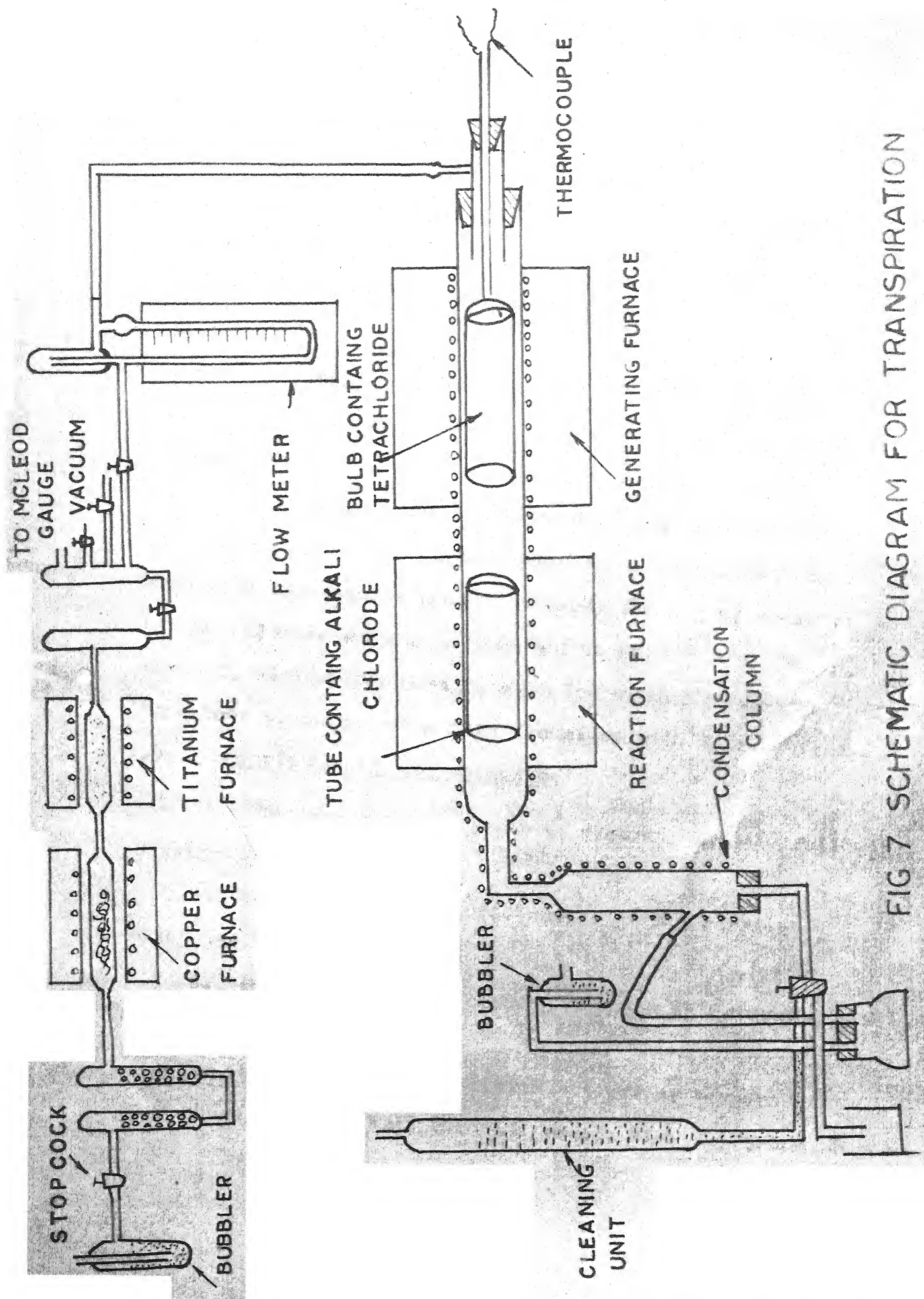
FIG 7 SCHEMATIC DIAGRAM FOR TRANSPIRATION TECHNIQUE

as to get a definite partial pressure of the tetrachloride
under the given experimental conditions. The temperature
of the alkali chloride can be maintained at any level.

3   The excess tetrachloride vapours are allowed to
condense in seperate condensation unit from where it can
washed off.

4. The technique also has provision for allowing
measurements of the steichiometry of the substance after
reaction.

The transpiration technique has wide applicability
and its accuracy is often reported to be excellent.This
technique can also be used to measure the vapour pressure
of the volatile compounds provided it is not very low.
However, with proper design, even low vapour pressures
have been measured using this technique with fair accuracy.

3.3   Description of the apparatus

The apparatus as shown in figure 7 has the following
distinct parts

1. The gas train for purification of the carrier
Argon gas.

2. The generating furnace where Argon is saturated with
the tetrachloride vapours.

3. The reaction chamber with a constant temperature
zone where in the alkali chloride reacts with the tetrachloride.

4. The cleaning unit for cleaning out the condensed tetra-chloride.

Argon is purified by passing it through a calcium chloride tower and over heated titanium powder. The flowing carrier gas is saturated with tetrachloride gas vapours in a generating chamber, the temperature of which is maintained constant. The tetrachloride vapour then passes through the reaction chamber where it comes in contact with alkali chloride particles kept in a tube closed at its end by glass wool. Any organ gas, escapes through a sulphuric acid bubbler. The flow rate of argon gas is monitered by a gas flow meter attached to the system immediately after the gas train.

In order to obtain reproducible results in the experiments using transpiration technique, it is absolutely essential to specify the flow rate of the carrier gas and the geometry of the system. The flow rate must be sufficiently slow to ensure that an equilibrium pressure of the tetrachloride vapour is established in the system. At very slow flow rate diffusive flow of vapour becomes predominant than convective flow, which is not desired as it leads to uncertainities in the pressure of the tetrachloride gas. At very high velocities, on the other hand, the apparent partial pressure measured is low because of non-equilibrium conditions. Any predetemined flow rate of the gas is ensured

by maintaining a constant liquid height difference in the arms of the flow meter. The tetrachloride saturated gas flows through the system. The partial pressure can be calculated for each run in the following way

suppose the loss in weight of $ZrCl_4$ = X in one hour.

Number of modes of $ZrCl_4$ lost $= \dfrac{X}{233.05}$

Let the flow rate of Argon $= y$ cc./ min.

Total number of moles of Argon passed $= \dfrac{y.1.60}{1000 \times 224}$ / hr.

$$\text{Partial pressure (mm)} = \dfrac{X/233.05}{\dfrac{y\,60}{1000\ x224} + \dfrac{x}{233.05}} \times 760 \qquad (17)$$

This experiment is repeated for different flow rates of the carrier gas. The results of these experiments are shown in figure 8. With the help of figure 8 the optimum flow rate of the gas is determined as also the time allowed for the reaction. The rate employed in present set of experiments has been 176 cc/ min. and a reaction time of one hour is chosen for the partial pressure effect runs.

.4 Distillation of Zirconium Tetrachloride

Before the start of a set of runs the tetrachloride was distilled so as to remove impurities, if any. The distillation apparatus consisted of a long one end closed pyrex tube attached to a vacuum line as shown in figure 9.
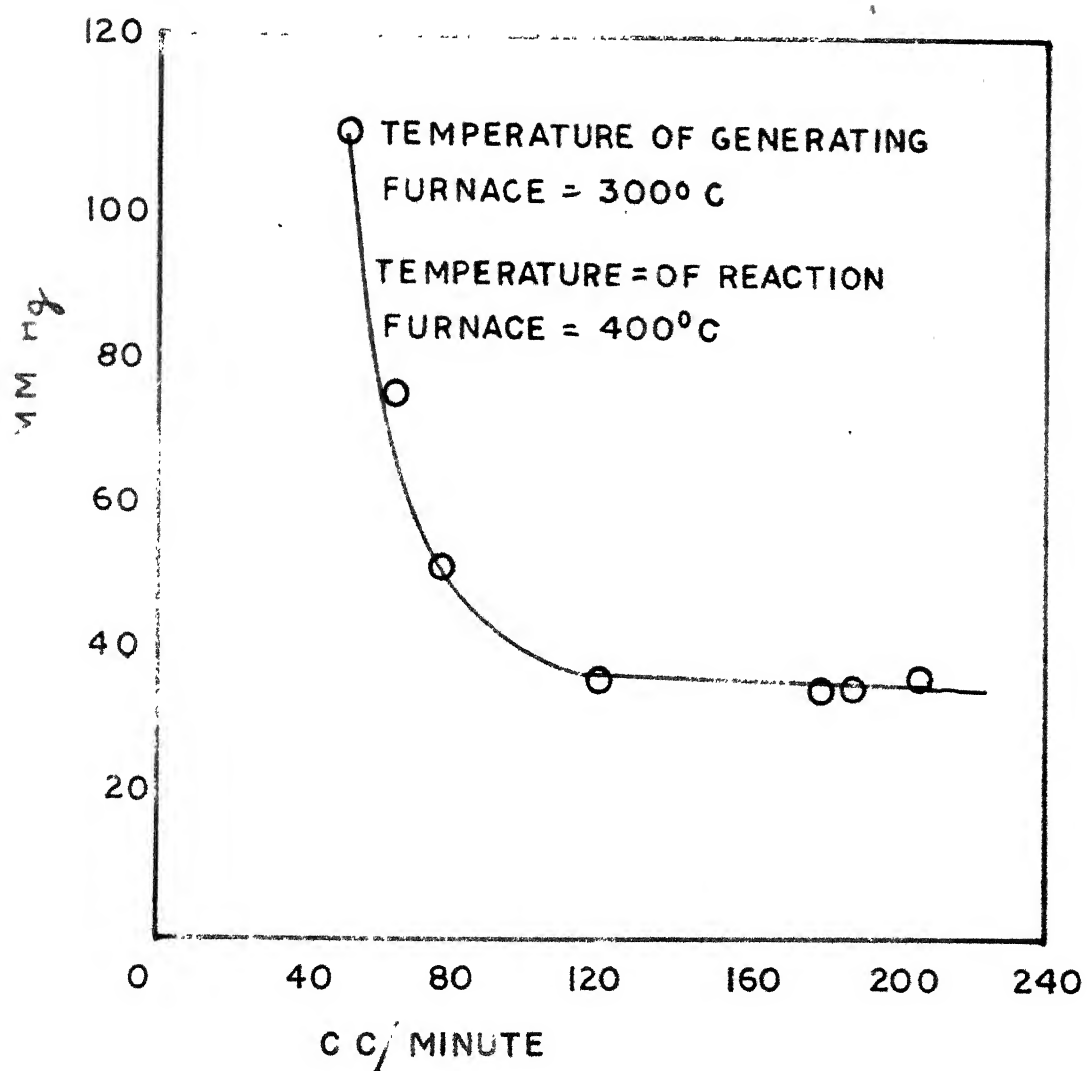
G 8 FLOW RATE DETERMINATION FOR MINIMUM P_{ZrCl_4}

The tetrachloride was introduced inside the tube in a dry box under inert atmosphere of Argon. On top of this some copper filings were filled and finally it was seperated from being sucked in the system by a lump of glass wool. This tube was then sealed and connected to a vacuum line. The system was then thoroughly evacuated at about 160°C with the tetrachloride end being inside the furnace for about 20 minutes to remove the gases . Then this tube was further heated to 325°C. This resulted in vapourisation of the tetrachloride which condensed in the cooler regions of the tube exposed to the atmosphere. This distillate was again taken out in a dry box and redistilled once more and then filled in the pyrex glass bulb and sealed with wax.

3.5 Experimental procedure in the transpiration technique

Kinetic investigations with polycoystalline alkali chloride particles, need standardization of the procedure to compare the results of studies with different alkali chlorides or mixture of alkali chlorides. The following standard experimental procedure is employed:

The copper furnace was heated to 425°C while the titanium furnace was heated to 700°C. The temperature in the generating furnace was set at 300°C while the reaction furnace was heated to 400°C and thus maintained for atleast two hours before the start of the experiments.
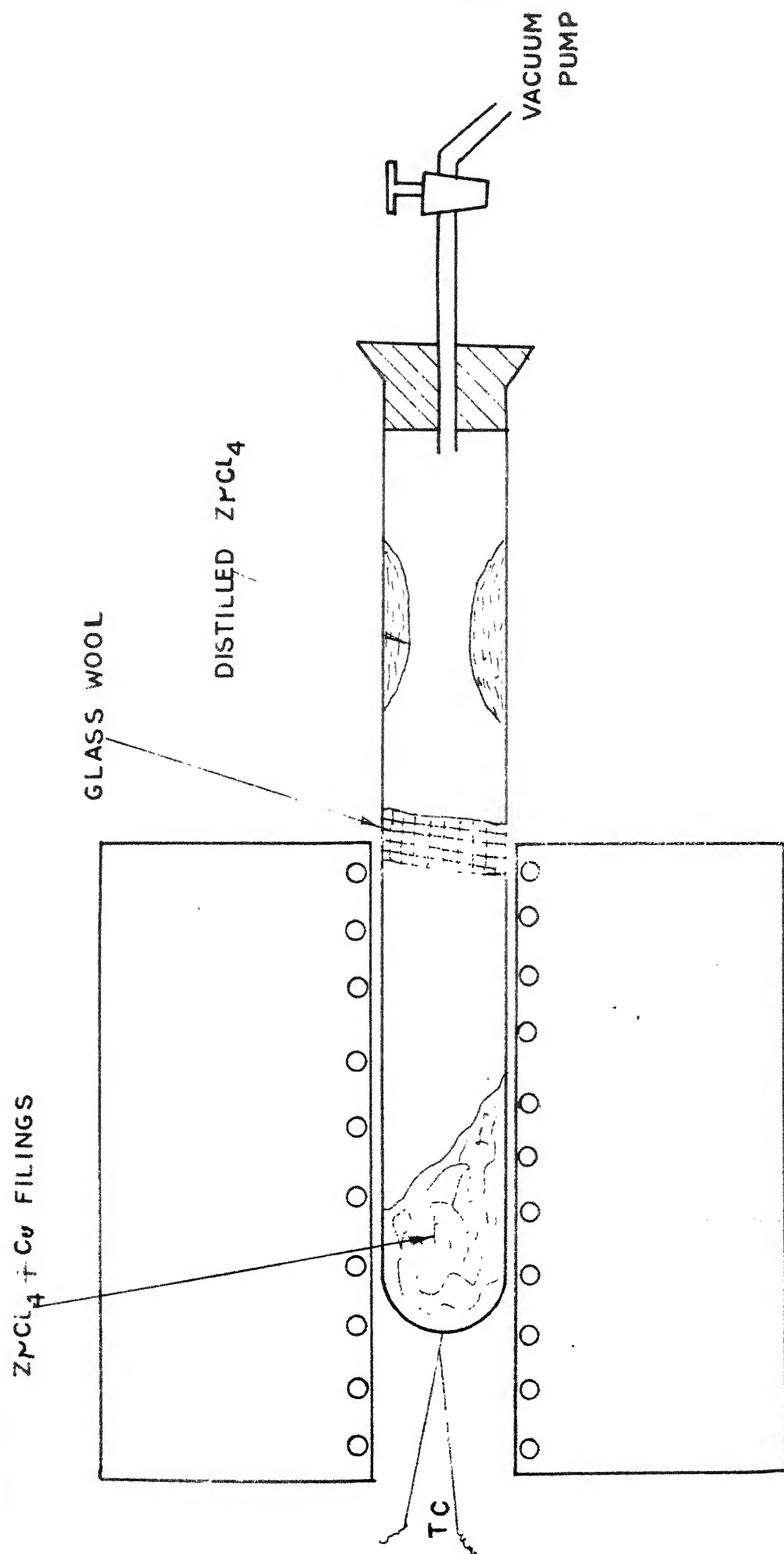
FIG 9 APPARATUS FOR DISTILLATION OF $ZrCl_4$

VACUUM PUMP

DISTILLED $ZrCl_4$

GLASS WOOL

$ZrCl_4$ + Cu FILINGS

TC

Having ensured that all the four furnaces were at the required temperature, the entire gas train was evacuated upto 50 micron pressure and then the carrier gas was slowly admitted through it in stages so as to finally reach the reaction and condensation chambers. This flushing was continued for 2 hours. Flow rate of argan was kept constant at 176cc/min. during the temperature pressure effect runs but varied during the temperature and time effect runs.

Solium chloride particles were filled in a glass tube and closed the end with glass wool plug. The length of the chloride bed was about 25 mm. This tube was weighed empty and after the NaCl filling to determine the weight of NaCl. This tube was then pushed inside the reaction chamber in the constant temperature zone. Solid $ZrCl_4$ was taken in a pyrex glass tube open at both ends but with ends plugged with glass wool and then placed in the constant temperature zone of generating furnace after weighing. Immediately argon gas was admitted after being preheated in the gas train. $ZrCl_4$ sublimes at 280 °C and gives out $ZrCl_4$ vapours which are carried away by the argon gas. These vapours of $ZrCl_4$ pass through the bed of NaCl and react thereby to form sodium hexachlorozirconate.

The reaction of $ZrCl_4$ vapours with NaCl is continued for constant time period during the pressure effect runs but varied for temperature and time effects. Also for temperature

effects the temperature in the reaction furnace was changed to 350°C, 400°C ,and 450°C. Similarily for time effects keeping the pressure and temperature constant in both the generating and reaction furnaces, the period of the reaction was varied.

After completion of every run, the $ZrCl_4$ bulb was taken out and stoppered. The tube containing sodium chloride was taken out and kept in a dessicator for cooling. After cooling both these tubes were weighed again to determine the loss and gain in weight respectively.

For the weight gain experiments for NaCl-KCl mixtures the data was taken after a suitable mixture of these by weight percents was kept inside the reaction furnace and the procedure repeated with $ZrCl_4$ bulb as above.

Preliminary results showed that the extent of solid

gas reaction under the conditions of the present investigations

is very small. For such limited extents of reactions Jander's

model should be applicable for single spherical particles.

For a bod of 'n' particles, assuming each to be a

sphere then each particle will react to the same extent for

a given set of conditions. Jander's equation is

$$\left[1-(1-F)^{1/3}\right]^2 = K_j \cdot t$$

i.e. $F = 1 - (1 -\sqrt{K_j \cdot t})^3$

when 'n' particles react, we have $F_1 = F_2 = F_3 \cdots = Fn$

$$nF = n\left[1 - (\sqrt{K_j \cdot t})^3\right]$$

i.e. $F = 1 - (1 -\sqrt{K_j \cdot t})^{3/1}$ (18)

This equation indicates that the same Jander's equation

is valid for a packed bed also provided

a) Each polygonal particle be assumed to be a sphere,

b) The extent of reaction be so small that each particle

retains its identity and surface area.

4.1 Establishment of a fixed P_{zrCl_4} in flowing gas stream.

Graph shown in figure 10 gives the weight loss
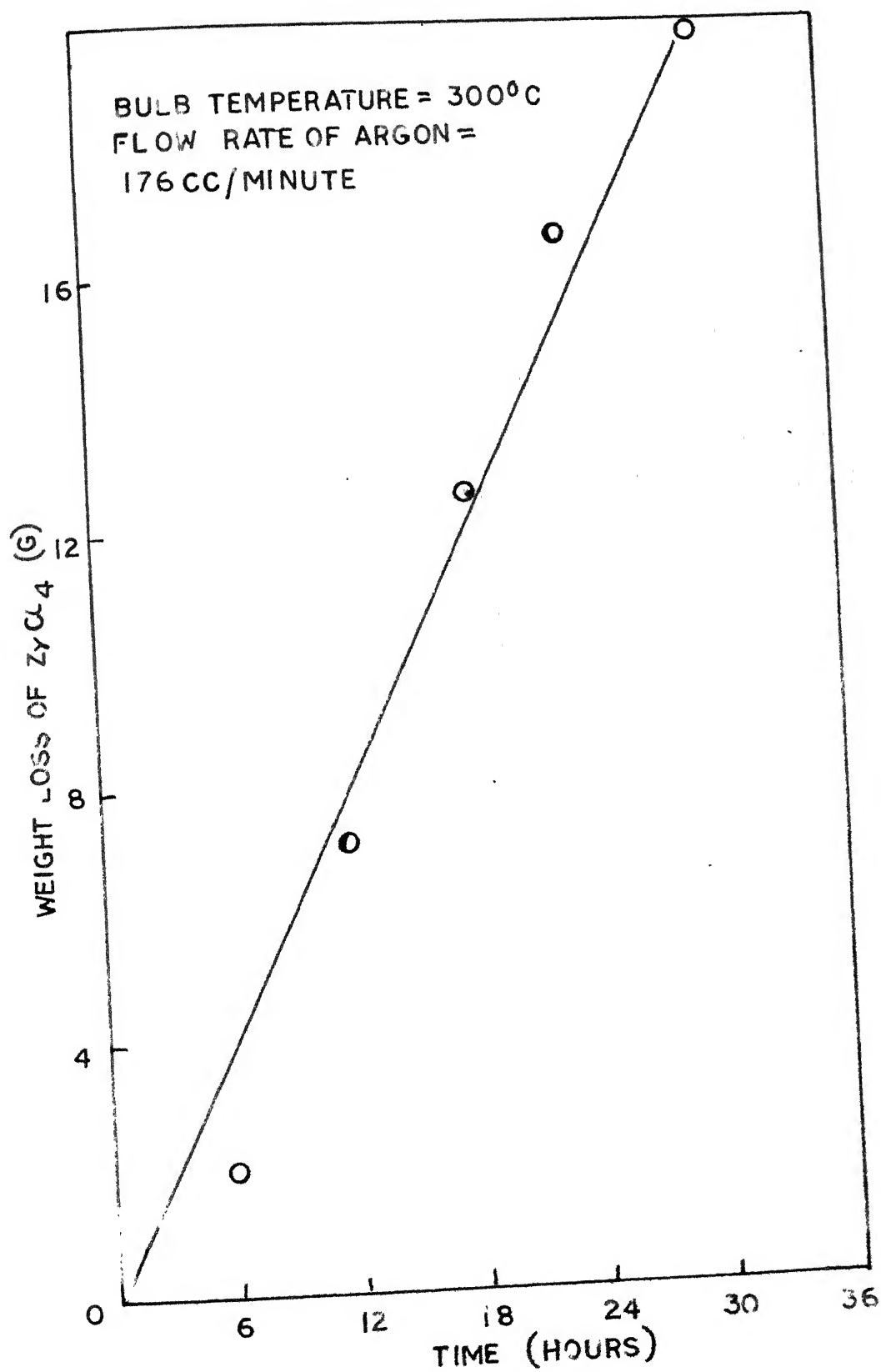
FIG 10 WEIGHT LOSS OF ZrCL₄ VERSUS DIFFERENT PERIODS OF TIME

from a $ZrCl_4$ filled bulbs versus for different priod of time.
Each point corrosponds to an entirely independent run. It
should be noted that the $ZrCl_4$ filled bulb cannot be reins-
erted once it has been taken out for weighing to measure the
weight loss. It also been observed that the $ZrCl_4$ surface
tends to become inactive while in the process of being taken
out without measurable change in weight. The figure clearly
shows that the rate of weight loss is almost reproducible
from run to run and remains uniform at least as long as
30 hours provided that the geometry of the system, the flow
rate of carrier gas and the temperature of the bulb remains
constant. It is therefore concluded that the partial pressure
of $ZrCl_4$ is uniquely defined by experimental conditions.

4.2   Effect of time

The effect of change of time on the reaction
rate is shown in figure 11. The ~~rate constant~~ term $[1-(1-F)^{1/3}]^2$ varies linearly
for very low extents of reaction and thus satisfies Jander's
model.

4.3   Effect of temperature

The effect of change of temperature of the
reacting zone on the specific rate constant is shown in the
figure 12. Here the Arrhenius type of equation relating the
rate constant to the temperature of the reaction is plotted.

FIG II EFFECT OF TIME ON REACTION RATE

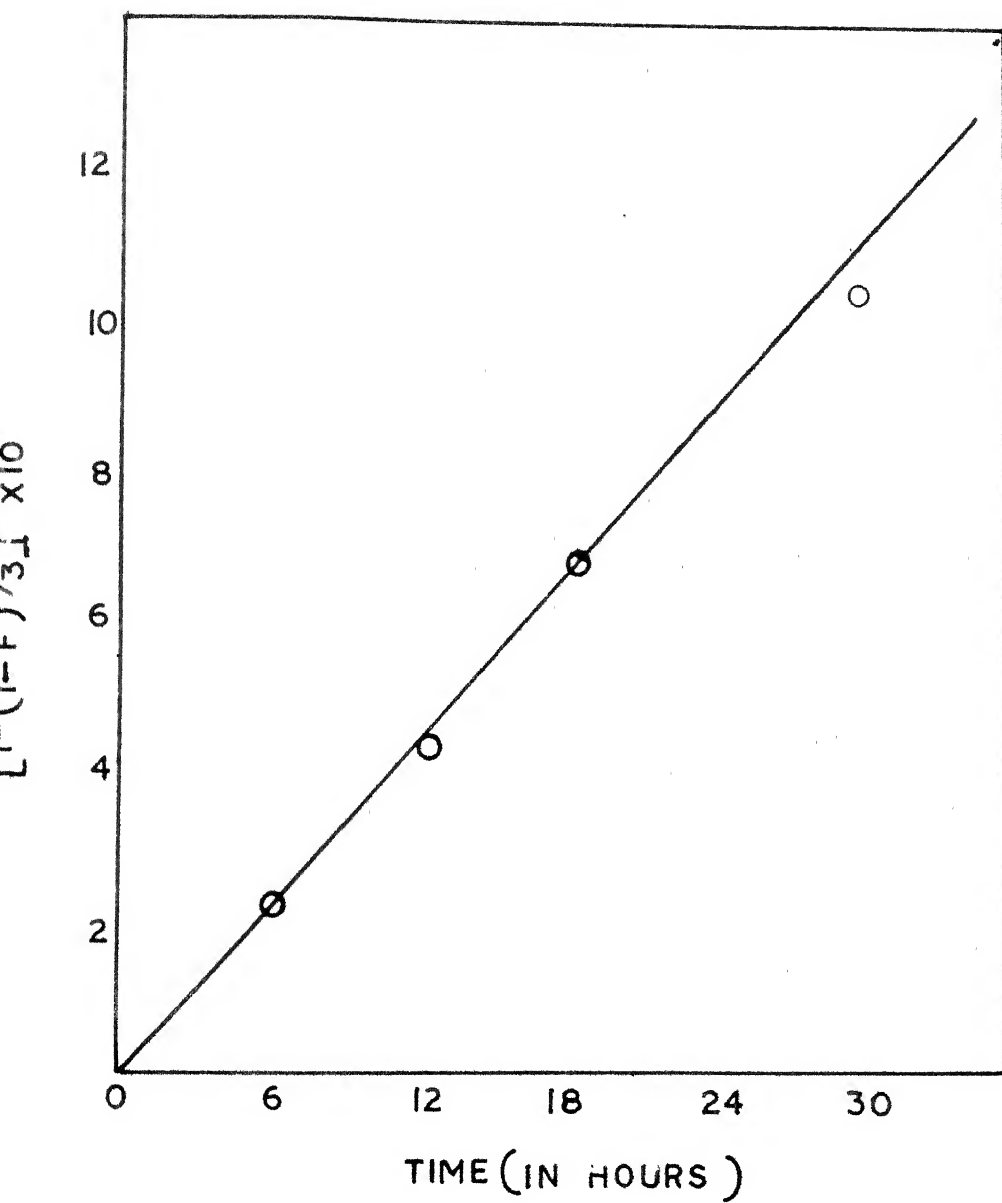FIG 12 EFFECT OF TEMPERATURE ON REACTION RATE

TEMPERATURE OF GENERATING FURNACE = 300° C

FLOW RATE OF ARGON = 176 CC/ MINUTE

4. 595 X SLOPE = E
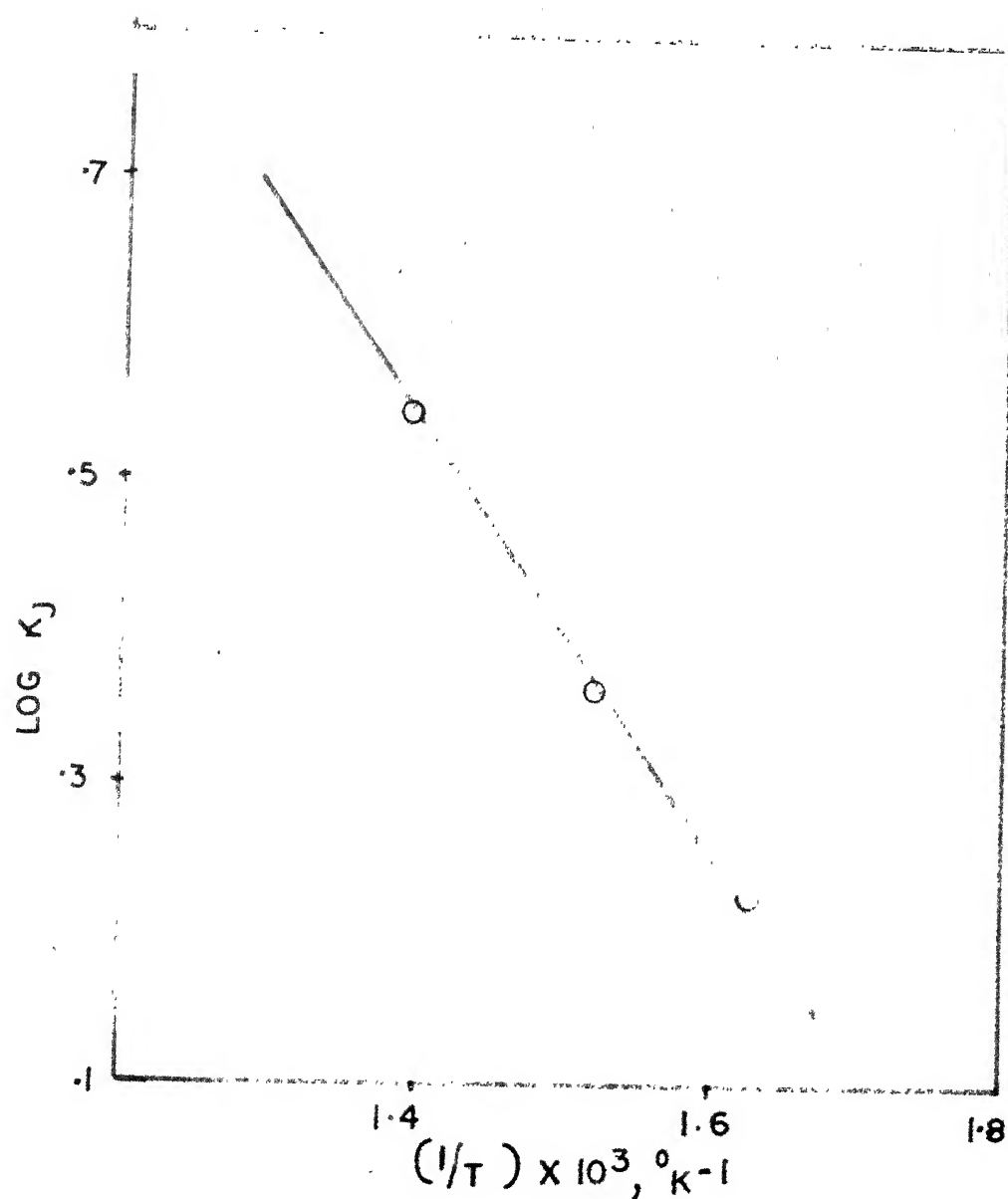
FIG 13   MEASUREMENT OF ACTIVATION ENERGY

From the measured slope of the linear plot the temperature coefficient (apparent activation energy) of $ZrCl_4$ - NaCl reaction in the temperature range 350°C-450°C is computed in the figure 13. This measured to be 6.9 Kcal/Mole. Earlier Luthra and Mazumdar, using the single sphere technique obtained values of 9.9 and 7.5 Kcal./mole respectively in 440-480°C temperature range.

4.4 Effect of pressure

The effect of tetrachloride pressure on the rate of formation of Na_2ZrCl_6 is shown in figure 14(a). It suggests due to its linearity, a power relationship between the gas pressure and rate constants. Empirically the pressure of effect can be represented by

$$K_j \propto p^{1/n} \qquad (19)$$

Where pressure coefficient 'n' has a value of ~~1.63~~ 1.08 at 400°C for Zirconium. This value of n was obtained from the slope of the graph 14(b). Pint and Flengas had studied the effect of pressure and reported the zirconium reaction to follow $1/2.8^{th}$ power at 480°C and Luthra reported 'n' to be equal to 2.4 at 500°C whereas Mazumdar reports it as 1.98 at 450°C.

4.5. Effect of addition of potassium chloride:

The weight gain effect for KCl and NaCl mixture is shown in figure 15. One might expect a linear variation
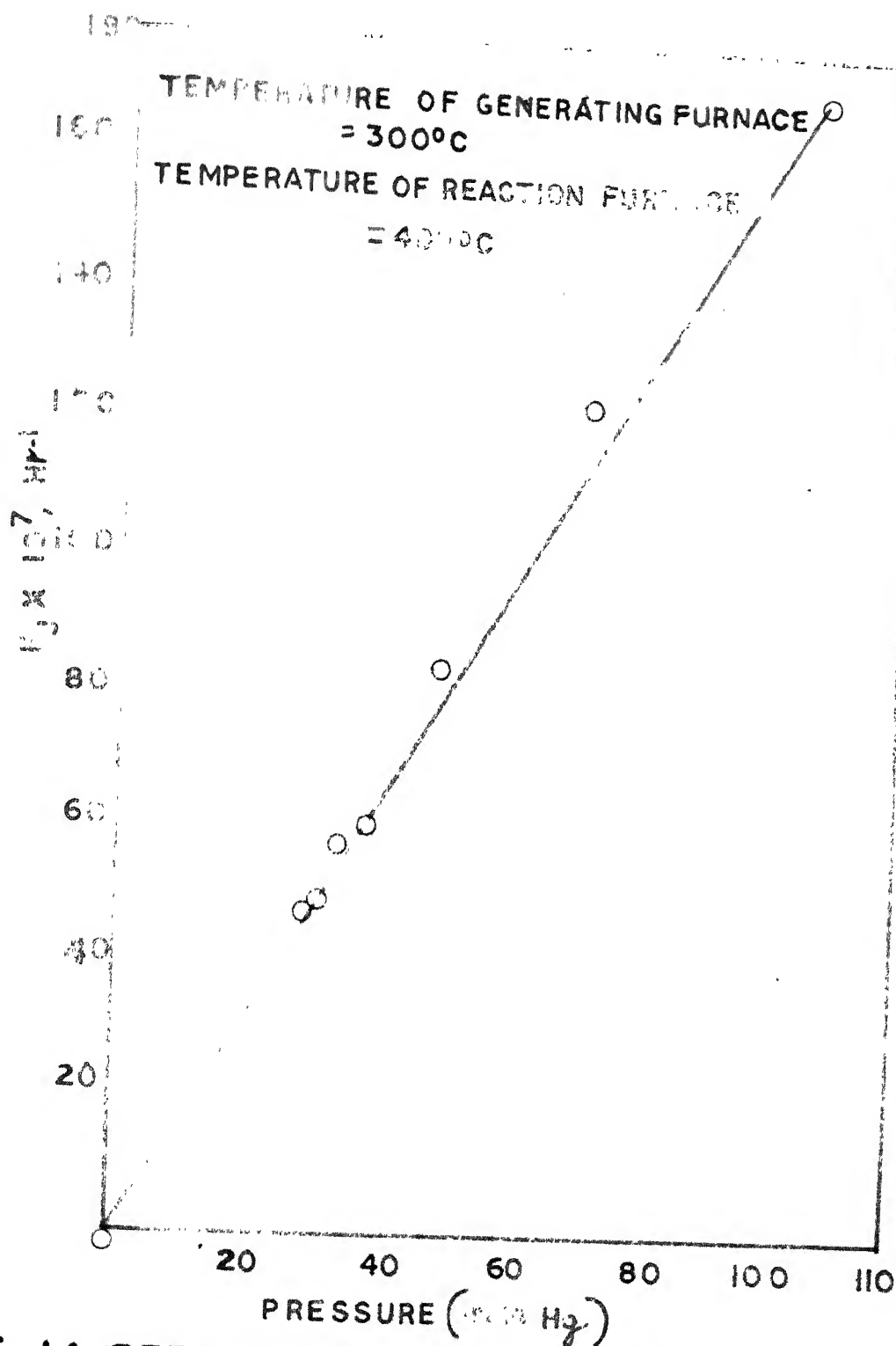
FIG 14a EFFECT OF PARTIAL PRESSURE OF Z_YCl_4
REACTION RATE
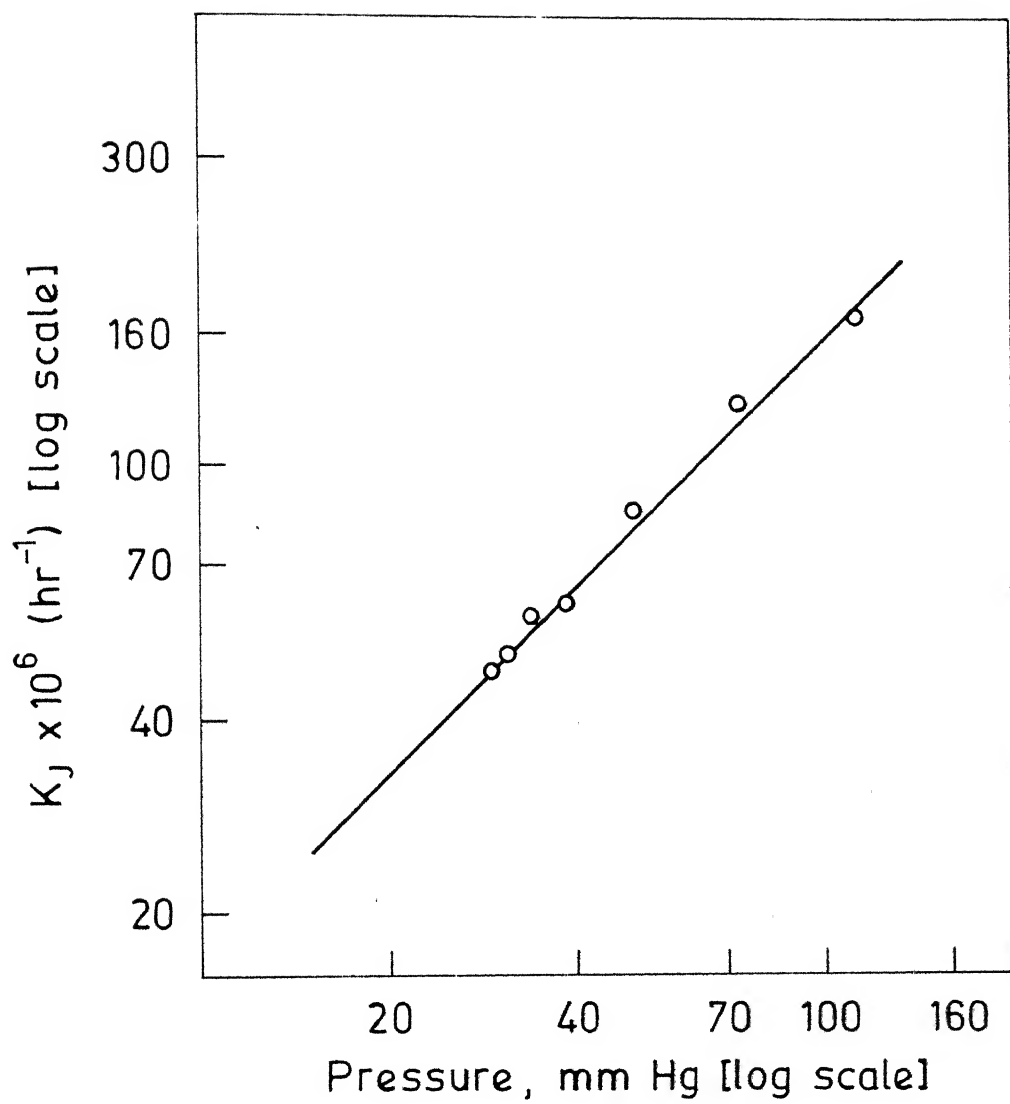
Fig.14(b) Effect of pressure on reaction rate.

(algebraic summation). As in the case of Bhat, the phenomenon is explained on the basis of overheating. It is attributed to the exothermic nature of reaction for hexachloride formation thus leading to local overheating and consequent increase in reaction rate. Also overheating causes localized melting to produce liquids of uncertain compositions. In this case the gas reacts faster with material. Also it does not match with Bhat to the extent that in his case two peaks are found occuring consequently whereas here the second peak appears at the KCl rich end.

Figure 16 shows the diagram for NaCl-KCl system. It is noted that the experiments are conducted at the temperature of 400°C for which the phase diagram does not show a complete solid solution throughout. But it is to note that the peaks are obtained both in the regions where there is a change over from the solid solution to the crystalline phase and vice-versa. The system itself being a complex one and in absence of detailed information of various compounds and solutions involved no definite explanation can be given.

Even though definite conclusions cannot be drawn from the results with mixtures of polycrystalline particles a very important observation different from the earlier ones stands out as follows :

1) Small additions of KCl (upto 10 weight percent)
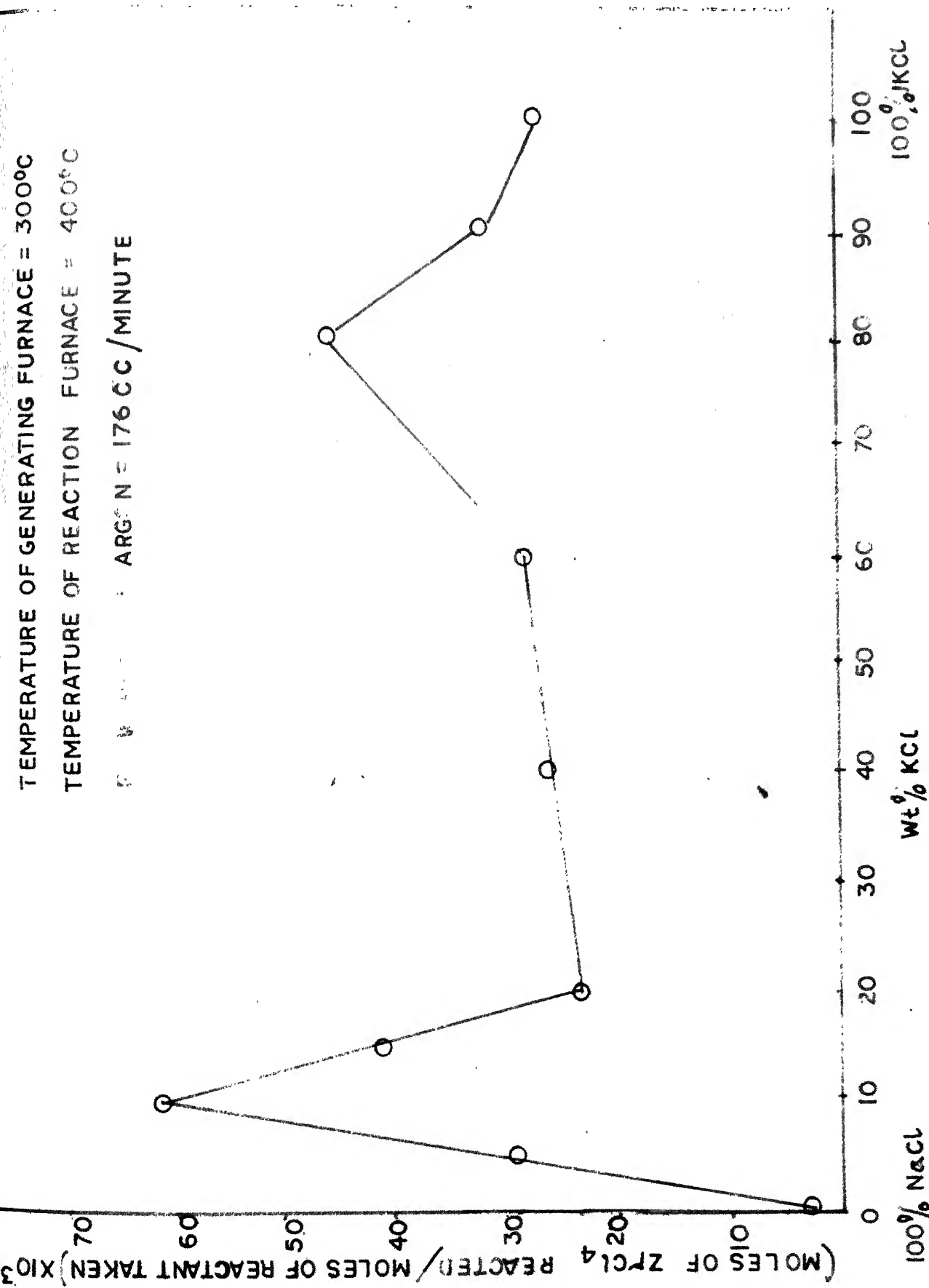
FIG 15 EFFECT OF KCL-NaCl MIXTURE

TEMPERATURE OF GENERATING FURNACE = 300°C

TEMPERATURE OF REACTION FURNACE = 400°C

ARGON = 176 CC/MINUTE
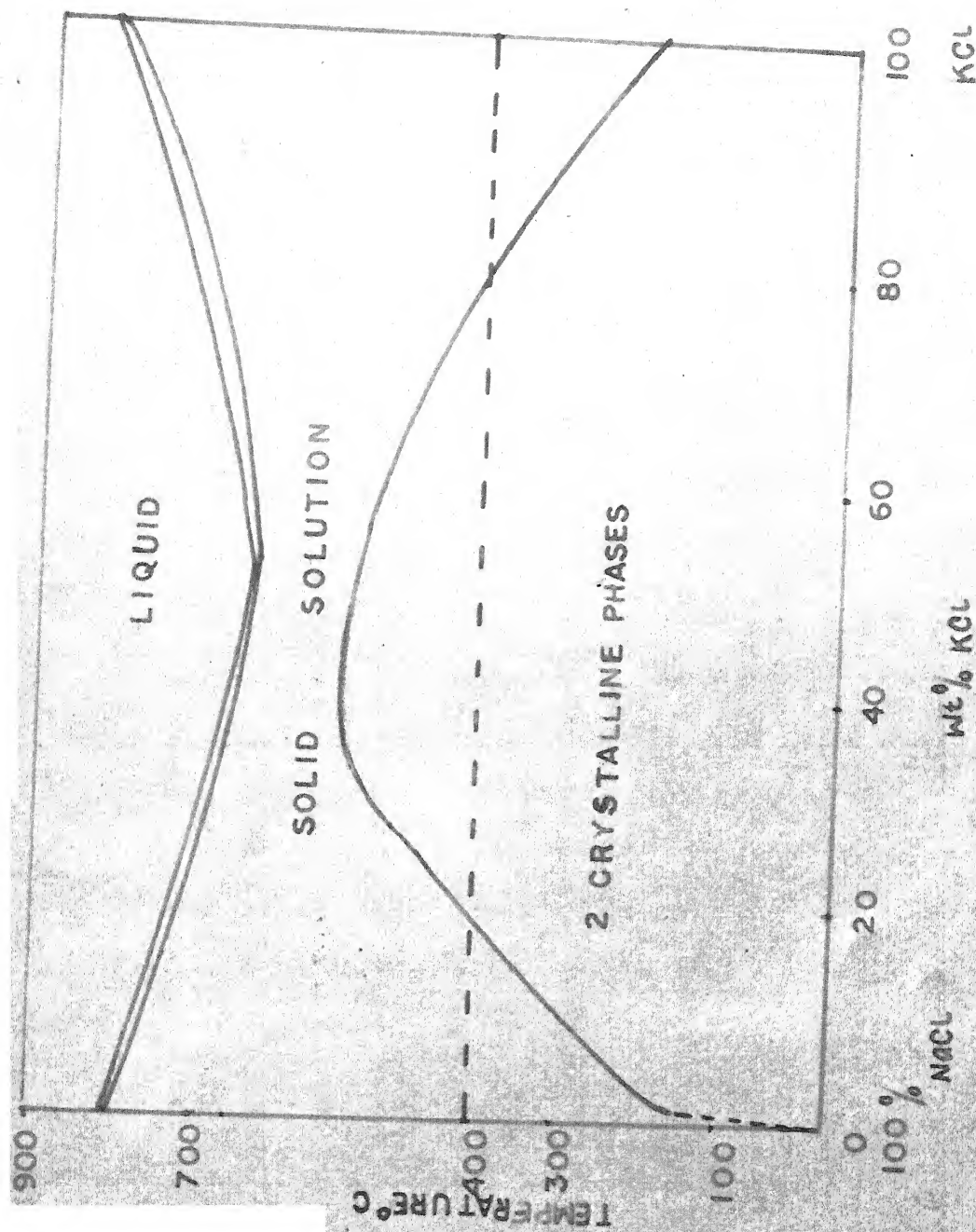
FIG 16   NaCl — KCL   PHASE DIAGRAM

in the NaCl mixture increases the reaction rate considerably.

2) Small additions of NaCl (upto 20 weight percent) to KCl mixture increases the reaction rate considerably.

3) Reaction rates are faster on the sodium chloride rich ends.

CHAPTER- FIVE

REACTOR DESIGN AND FABRICATION

Whenever a mixture of the vapours of zirconium tetrach-
loride and hafnium tetrachloride is passed a bed of sodium
chloride (or any other chloride) the unreacted mixture of
the vapour is enriched in zirconium. This can be attributed
to kinetically and energetically more favourable reaction of
hafnium tetrachloride with sodium chloride. The free engergy
changes for the reaction of these tetrachlorides with alkali
chlorides also determine that this seperation is thermodyna-
mically possible. Based on these arguments a reactor was
designed, fabricated and assembled.

Due to the reaction being heterogenous and extremely
slow in nature, a continuous exposure of fresh solid surface
to the gas phase, would help considerably in increasing the
reaction rate. Further as the reaction is assumed to be
diffusion controlled, the stripping of the product phase
from the solid phase would facilitate the contact of reactive
vapours with the unreacted core of the solid. Both purposes
e.g. continuous exposure of new surfaces of solids and conti-
nuous removal of the product phase from the unreacted core,
is achieved by a screw conveyor reactor. In a screw conveyor

the screw shaft rotates continuously forcing the solid parti-
cles to roll and collide all the time. The path of movement
is along the axis of the screw.

5.1 Design details

The reactor designed for the seperation is long
tube of inconel. Three feed inlets are provided for either
solid or gas. Two of these inlets are at the flange ends
and one in the middle of the tube length. The inlet tubes
are along the length in a simple row. To collect gas samples,
four tubes as gas sample collectors are provided at an angle
to the feed inlet and are spaced 30 cms.apart.

A screw shaft, which rotates inside the reactor
body, does the work for carrying the solid from one end to
the other. The flow of the solids can be changed by reversing
the direction of the screw shaft.sSolid sodium chloride can
be fed at one end from a reservoir and the tetrachloride
vapours are fed through the feed inlet along with the
carrier gas argon. The unreacted vapours of the tetrachloride
are allowed to condense in a condensor cooled with running
water. The solid flow through the reactor ends in a sink
through the outlet at the bottom end of the reactor. The
solid flow rate is controlled by regulating the rotation
of the screw whereas the vapour flow rate is controlled by
argon gas flow rate as well as the temperature of the
tetrachloride source.

The tetrachlorides being reactive vapours, special care is taken to see that these vapours do not come in, contact with water vapour of the atmosphere. Hence, the entire reactor is leak proof and the system does not come into direct contact with atmosphere.

As far as possible the temperature inside the reactor is maintained constant along the length of the reactor by properly providing the kanthal winding for heating along the surface length. The temperature profile is determined by using a thermocouple along the length of the hollow tube of the screw shaft.

The sample collectors are designed to incorporate cold fingers as shown in figure 17. One of the cold fingers is for the feed inlets while the other one is for gas sample collection. During normal operation no tetrachloride condenses on these. However, when, heating of the outlets is switched off and cold fingers are cooled by water flow, tetrachlorides are condensed easily.

Feeding of tetrachloride is by taking a standard bulb filled with a weighed quantity and pushed inside the feed inlet and stoppered. As it sublimates the vapours are carried along in the reactor by the argon gas flow, maintained through a gas train, at right angles to the feed inlet. This eliminates any possibility of forced carry over of the tetrachloride particles.

5.2   Fabrication

Various components of the whole reactor were fabricated seperately and assembled as per the drawing.

5.2.1 Reactor

The main reactor shell is made of two inconel tubes welded together. The diameter is 64 mm and the length between the flange ends is 900 mm. The feed inlets are made of stainless steel tubes 25 mm in diameter and 240 mm in length. These are welded to the reactor body at right angles. The sample collector are made of stainless steel tubes of 8 mm diameter and 150 mm long. These are joined parallel to each other, perpendicular to the reactor body and spaced 300 mm apart. The angle between the feed inlets and the sample collectors is 45 *.

Brass flanges having 'O' rings to act as sealing gasket are used to close the ends of the reactor body. Also 'Teflon bead' is put into further prevent the escaped of gases during operation.

5.2.2 Screw Conveyor

This comprises of a hollow stainless steel tube about 2.05, meters long and 100 mm in diameter on which a plate is twisted in such a fashion as to form a helical spiral around it which gives the movement like that of a screw. This screw is specially made from pieces

cut from stainless steel sheet of the size of 58 mm x 58 mm and 3.2 mm thick. In the centre of these pieces 10 mm diameter holes are drilled. Several of these squares are mounted on the mandrel of the lathe and machnined to make them circular discs of 50.5 mm diameter. These discs are cut along the radius and subsequently turisted as to form a helical fin. These fins are then mounted on the central tube and then welded welded to each other. Also ends of each fin is welded to the neighbouring end. This is continued for 1.5 meters along the length of the screw shaft. The edges of these fins were again ground so as to fit inside the reactor shell. The shaft is hammered straight after welding some length because of the bending due to heat.

5.3 Assembly

The screw shaft is fitted into the reactor and its flanged ends closed with 'O' rings and Teflon beads. The central hole at the flanges through which the screw tube passes also has a a Teflon ring fitted so as to avoid escape of gases. The whole reactor rests on a stand by means of three clamps bolted in the base plates of the stand.

The screw conveyor ends rest through two plummer blocks which support and provide, the bearing movement for rotation. These blocks are set upon two wooden blocks which are fixed to the base stand. One of the ends of the tube

has a handle fixed so as to provide material movement at a very slow r.p.m.of the screw.

Spcial heating arrangements are provided to the reactor so that reactions occur at high temperatures along with no condensation of tetrachloride inside the reactor. The reactor winding for heating is done in four segments. Two segments are between the flange ends and the two feed inlets and outlet. The other two segments are between these two feed ends and the centre feed inlet/outlet. All these segments are electrically fed through seperate var iacs. The kanthal heating element used is of 18 SWG, Swedish make. The sample collecting tubes and feed inlet tubes being thinner in cross section are heated with elements of higher resistance i.e. 28 SWG of Nichrome. Each of these heating sections are connected through seperate variacs.

The whole length of the reactor and the inlet and sample tubes were applied with a 2 cms thick layer of fire clay and corrunden paste so at to provide a refractory coating to the reactor. This layer is again covered by flexible asbestos sheets to provide an insulation against short circuiting. The heating element wound over this and then covered with refractory rope and cloth to reduce the radiation losses. A few extra rounds of wire heating elements per linear length is provided near the sample collector tubes

because of some are of reactor being not accessible for winding due to element crossing and thus compensate for heating loss.

Suggestions for experimental work

The determination for the feasibility of seperation of hafnium from zirconium depends upon a number of factors. All the conclusions drawn so far regarding this system have to be incorporated when taking up the study on the reactor. The entire process of seperation depends on how fast equilibrium conditions are achieved which is determined the kinetics of the reactions. Experiments should be conducted on the system to investigate the extent of reaction at the various stages of the reactor. For this, samples should be taken and analysed. This will help in assessing the extent of seperation acheived for any particular length of the reactor. This in addition defines the length of reactor as equivalent to a certain number of stages. Also the analysis of samples taken can determine the extent to which equilibrium has been acheived.

The following experiments should be performed on the reactor.

1. Fractional sublimation of $ZrCl_4$ using inert glass beads.

This will be a case of sublimation without reaction equilibrium.

2. Introduction of reaction equilibrium. For this $ZrCl_4$ sublimation and reacting it with sodium chloride particles.

3. Fractional sublimation with exclusive dependence on exchange reaction. Here Na_2ZrCl_6 particles should be introduced and hafnium tetrachloride vapours passed.

4. Exchange reaction between Na_2ZrCl_6 and Na_2HfCl_6 particles can be studied by allowing then to travel together with only carrier gas passing from feed inlet.

For kinetic studies following experiments should be conducted.

1. Fixed P_{ZrCl_4} vs flow rate should be established and a flow rate thus can be obtained at which low P_{ZrCl_4} can be attained. The change in pressure is incorporated by varying the temperature from $200°C - 300°C$.

2. Studies can now be conducted for rate of reaction of NaCl particles as a function of time, temperature of the reacter and partial pressure at which tetrachloride vapours are generated.

3. As has been observed earlier, the reaction is accelerated by addition of 10 % by weight of pottassium chloride, it should be confirmed by actual experiments and analysis of the sample. Also this may move the operation closer to equilibrium conditions.

Analysis of the samples is a difficult proposition because of the two elements hafnium and zirconium being similar in nature thereby having a very complex analytical process. Neutron activation analysis is comparitively exact' one and this technique shouldbe perfected for a more elaborate interpretation of the results. Preparation of samples obtained also is a area which requires a careful investigation. The tetrachloride gas is corrosive enough to cause harm to the apparatus.

CHAPTER - SIX

CONCLUSIONS

The present investigation shows that the kinetics of the reaction of tetrachloride vapours $Zr(or\ Hf)Cl_4$ with sodium chloride particles can be understood in terms of Jander's model. Accordingly plots of $[1-(1-F)^{1/3}]^2$ versus time are linear for given values of temperatures and particle size. The Jander's rate constant is found to vary linearly with pressure i.e. $K_J \propto P$.

As expected K_J increases with temperature and the various curves follow the well known exponential relationship. The activation energy is approximately 7 Kcal./mole. These observations are consistent with earlier work done in this laboratory.

It is also shown that unexpected results are obtained for the reaction of $ZrCl_4$ vapours with mixture of sodium chloride and pottassium chloride particles. Pure KCl reacts far more rapidly than pure NaCl. However reaction with mixtures

do not follow proportionally. Very high rates are obtained at about 10 weight percent KCl and about 20 weight percent NaCl mixtures.

A reactor has been designed and fabricated to acheive seperation of zirconium from hafnium based on fractional decomposition of the compounds Na_2ZrCl_6 and Na_2HfCl_6. A continuous exposure of new surfaces of the reacting solids with vapours and a continuous removal of product phase from the unreacted core is acheived in this screw conveyor reactor.

The reactor is an inconel tube having feed inlets and sample outlets. There is a screw shaft which rotates in the reactor with the help of bearings and thus exposes the solids to the vapours in the process of moving the solids from one end to another. This assembly is mounted on a stand. The reactor is insulated and wound with heating coils. Unreacted tetrachloride vapours flow out and condense in a condenser cooled with running water. Sodium chloride movement can be controlled by regulating the rotation of the screw and vapour flow rate by the flow rate of carrier gas. and the temperature of the tetrachloride source.

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AN APPENDIX - I

Results of experiments for pressure effect.

Particle size of NaCl -14+50 mesh
Temperature of gen.fce. 300°C
Temperature of reaction fce. 400°C
Time of reaction 60 mins.

Flow rate of Argon cc/min.	Weight lost by $ZrCl_4$ gms.	P_{ZrCl_4} (atm.)	P_{ZrCl_4} (mm Hg.)	W Weight of NaCl taken (gms.)	W' Weight gained by NaCl	Fraction reacted $F = \frac{W'}{7.Z}$ (.5016)	$K_J \times 10$
50.00	5.151	0.142	107.658	11.173	0.277	.012440	173.30
62.50	4.103	0.095	72.320	10.196	0.215	.010580	125.20
77.00	3.366	0.065	49.738	6.593	0.115	.008749	85.55
130.00	4.334	0.051	38.531	12.026	0.176	.007431	60.17
170.00	4.291	0.039	29.536	13.031	0.171	.006582	48.35
176.00	4.651	0.041	30.867	10.066	0.134	.006677	49.77
206.00	6.069	0.045	34.252	10.250	0.148	.007243	58.57

Size of NaCl -14 +50 me h
Flow rate of argon 176 c/min
Temperature of gen fce 300°C

APPENDIX II

Results of experiments for temperature effect

Sl. No.	Temp. °C	Time (hr)	Weight of NaCl taken (gms)	Weight gained by NaCl (gms)	Fraction Reacted	$K_p \times 10^6$ $[1-(1-F)^{1/3}]^2 \times 10^6$
1.	350	6.0	12.937	.289	.01121	14.06
2.	350	10.0	13.123	.364	.01391	21.71
3.	350	20.0	11.346	.447	.01576	45.97
4.	400	6.0	10.200	.270	.01328	19.76
5.	400	10.0	12.184	.387	.01593	28.51
6.	400	25.0	13.328	.684	.02575	55.99
7.	450	6.0	11.062	.327	.01483	24.67
8.	450	12.0	9.335	.369	.01983	44.27
9.	450	18.0	11.176	.547	.02455	68.09
10.	450	30.0	10.083	.646	.03214	117.30

APPENDEX III

Temperature of gen.fce. 300°C
Temperature of reaction fce 400°C
Flow rate of argon 176cc/min

Results of experiments with (-14 +50 × h) mixture of NaCl and KCl

Sl No.	Wt % KCl	Mole % KCl	Wt % NaCl	Mole % NaCl	Weight of reactants	No. of moles reactants	Weight gained during reaction	Nos. of moles ZrCl₄ reacted	ZrCl₄ reacted per mole of reactant taken
1.	0	0	100	100	12.2658	0.20986	0.12226	0.00052	.0025
2.	5	3.96	95	96.04	12.9387	0.21898	1.53098	0.00657	.0300
3.	10	8.01	90	91.99	12.7685	0.21374	3.13816	0.01347	.0630
4.	15	12.15	85	87.85	12.3978	0.20525	2.03285	0.00872	.0425
5.	20	16.39	80	83.61	11.9986	0.19642	1.09857	0.00471	.0240
6.	40	34.32	60	65.68	12.1052	0.18921	1.19058	0.00511	.0270
7.	60	54.04	40	45.96	12.8100	0.19076	1.19923	0.00553	.0290
8.	80	75.33	20	24.17	12.9786	0.18365	2.03294	0.00872	.0475
9.	90	87.57	10	12.43	11.9968	0.16316	1.25476	0.00538	.0380
10.	100	100	0	0	11.9178	0.15985	1.04309	0.00448	.0280